

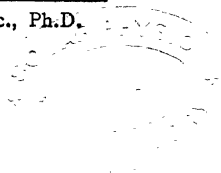
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FINE STRUCTURE IN LINE SPECTRA AND
NUCLEAR SPIN

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by

S. TOLANSKY, PH D , D I C , A I N S T P

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PREFACE

THIS book is meant as an introduction to the study of fine structure in line spectra for those who are already familiar with the elements of spectroscopy. The study of fine structure has already led to many important facts concerning the constitution of atomic nuclei, and will certainly lead to more. It is hoped that this short survey will prove useful to the student who contemplates undertaking research in this branch of the subject. The experimental and theoretical material is accumulating at a very rapid rate, so that no claim to completeness can be made, but the more important facts known up to date have been included. It has not been considered advisable, because of lack of space, to treat the Zeeman effect in detail, so that only a brief summary is given in an appendix.

I take this opportunity of expressing my thanks to Dr W. E. Williams of King's College, London, who has completely revised the manuscript and made many valuable and helpful suggestions.

I also wish to thank Miss E. Pincasovitch, who has kindly executed all the diagrams for me.

S. T.

IMPERIAL COLLEGE OF SCIENCE,
LONDON, *February*, 1935

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FINE STRUCTURE IN LINE SPECTRA AND NUCLEAR SPIN

CHAPTER I

INTRODUCTION

It has been known since the closing years of the last century that some of the lines of the spectra of a number of elements were not single lines. When examined with high resolving power instruments they were found to be complex groups of lines, and this complexity has been termed the fine structure of the line in question. A complex line may consist of a number of components, the intensities and spacings of the components not necessarily showing any apparent regularities. These structures have been a puzzle to spectroscopists for many years.

Recently the study of the fine structures of spectral lines has assumed more and more importance, for it has been shown that these structures are due, either to the existence of different isotopes, or else to the fact that the atomic nuclei themselves are associated with a spin. A careful analysis of fine structures has led to the discovery of very important facts concerning the constitution of atomic nuclei themselves.

Since the physics of the nucleus promises to be one of the most fruitful fields of investigation, it is worth while to mention very briefly the different methods that have been developed for attacking the problem of the nucleus. These may be broadly classified into three main methods, namely (a) Radioactive, (b) Magnetic (c) Spectroscopic. It is not the purpose of this book to deal with (a) or (b), but they will be briefly mentioned. Radioactive experiments first proved the existence of a small massive nucleus

in the atom, and then showed that the heavier radioactive elements have ionised helium atoms as constituents. It has recently been demonstrated that the neutron, which is an uncharged combination of electron and proton, is also one of the building stones of the nucleus and evidence of the existence of a positively charged electron has been recently discovered. The magnetic method of studying the nucleus has not yet been fully developed, and all that need be said is that the magnetic properties of the nucleus itself will contribute an effect in the Stern-Gerlach experiment of deflecting atoms in non-uniform magnetic fields.

The purpose of this book is to discuss one of spectroscopic methods, namely that of fine structure in the line spectra of atoms. Spectroscopy has developed two quite distinct lines of attacking the problem of nuclear structure, which strictly lead to different nuclear properties. The first method is to measure alternations of intensities which occur in many band spectra. Line spectra are emitted by electron transitions in *atoms*, while band spectra are produced by electron transitions in *molecules*. The simplest type of molecule is the homogenous type, consisting of two similar atoms, e.g. O_2 or N_2 . Oxygen and nitrogen have more than one isotope, but homogeneous molecules are those in which the two constituent atoms are similar, e.g. O_{16-16} and N_{14-14} , so that while the molecules O_{16-17} and N_{14-15} are oxygen and nitrogen molecules respectively, they are not homogeneous. When a homogeneous molecule emits a band spectrum it is found that the intensities of alternate lines of the rotation spectrum bear a fixed relation to each other. Theory shows that the alternations in intensity are due to the fact that each of the constituent nuclei of the molecule possesses a mechanical spin which is some small multiple of $\frac{h}{2\pi}$, h being Planck's constant. The numerical value of the intensity ratio depends upon the spin $I \frac{h}{2\pi}$, where I is a simple number which is called the nuclear spin. The alternations in intensity are purely

statistical effects and arise because the nucleus possesses a mechanical moment. Experiment shows that the hydrogen nucleus which is a single proton has a mechanical moment $\frac{1}{2} \frac{h}{2\pi}$, that is $I = \frac{1}{2}$ for the hydrogen nucleus.

It has been found that the nuclear spins, even of heavy atoms, are either zero or small half integral multiples of $\frac{h}{2\pi}$ (excluding the case of nitrogen and H^2 for which $I = 1$); it cannot therefore be assumed that the whole nucleus spins like a top, and the reasonable assumption has been made that only a small limited number of the nuclear particles possess this property. Since the spinning particles have an electric charge, one would expect that, in general, a magnetic moment should be associated with the mechanical moment. This magnetic moment couples with the magnetic moment of the valency electrons of the atom and the terms of the line spectrum are split up into two or more energy levels. The *terms* of a spectrum are due to the various possible orientations and values of the external electron magnetic moment, and the splitting up, or "*fine structure*," as it is called, due to the nuclear magnetic moment.

The magnetic moment of a spinning nuclear proton is approximately two thousand times smaller than that of a spinning electron because of the large mass difference, so that the intervals between fine structure terms will be very much less than those between the ordinary "gross structure" terms of the spectrum. It is at once apparent that the examination of fine structures can give information both about the mechanical and magnetic nuclear moments. Furthermore, very valuable data about isotopes have been deduced.

The measurement of fine structures in line spectra presents a number of experimental difficulties, due mainly to the minuteness of the scale of the structures. Observed fine structure separations vary from about 2 cm^{-1} to 0.010 cm^{-1} , but much smaller structures must occur which

cannot as yet be measured. With such close lines, a large dispersion combined with high resolving power becomes essential, while a too powerful excitation of the source will widen the lines beyond their natural widths, which may become of the same order or even greater than the fine structure separations. The term "fine structure" has, in the past, been somewhat loosely employed to denote the structure of a close group of lines which in a low power spectroscopic may appear as a single line. The complexity may be due to intrinsically different causes.

The ordinary "multiplet" lines due to the existence of two or more valency electrons are, in most spectra, sufficiently widely separated that they can be resolved with the lowest power spectroscopic. In certain instances this separation may be so small that it requires extremely high resolving power instruments to detect it. In order to distinguish the complexity of a line which arises from a purely nuclear effect (whether due to spin or isotopy) the term "hyperfine structure" has been frequently employed. To avoid unnecessary printing, this is simply referred to as "fine structure," while "gross structure" is employed in connection with multiplets in any cases when confusion might arise.

CHAPTER II

WIDTHS OF SPECTRAL LINES

IN general the fine structure components of a line lie very closely together and care must be taken to employ sources which will give narrow lines. For a hot arc in air, or a condensed vacuum discharge, line widths of the order of 0.1 cm^{-1} are not unusual. Such lines cannot be investigated if the structures are narrow, since the individual components are so broad that they overlap and cannot be separated, no matter how high the resolving power of the instrument may be. Several independent factors contribute to give finite widths to spectral lines and these will be briefly considered.

Doppler width.

Since the atoms which emit the observed light possess different velocities of thermal agitation, an observed line consists in reality of a band of frequencies. The velocities of the atoms correspond to a Maxwellian distribution curve. If the atoms emitted a truly monochromatic radiation, the effective observed wave-length of the light emitted by atoms moving towards the observer is decreased, and the observed wave-length of the light given out by atoms moving away from the observer is increased. This alteration in wave-length is proportional to the velocity of the particular atom in the line of sight, so that instead of an infinitely narrow line, a broadened line is observed, and the intensity distribution in the line is the same as the distribution of the velocities in the Maxwell curve.

A measure of the breadth of a line is its width at the point corresponding to half the intensity of the maximum.

It can be easily shown that the thermal width of a line is proportional to $\sqrt{\frac{T}{m}}$, where 'T' is the absolute temperature and m the mass of the atom emitting the radiation. The width due to thermal agitation becomes a very serious factor in the case of the lighter elements, and it can be reduced by cooling the discharge tube with liquid air.

Reversal

It frequently happens that the radiation from a hot source passes through a cooler layer of the same vapour and as a result the central radiations of some lines are partially absorbed. The amount of absorption depends upon the number of atoms in the cooler vapour which are in states

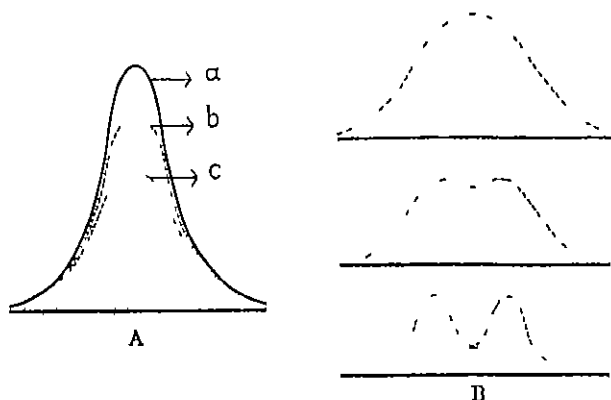


FIG. 1.—A Shows how a line is broadened by self-absorption
B Shows how further self-absorption produces reversal

suitable for absorption, so that the effect varies with different lines and different excitation conditions. At first the only result of absorption is the apparent broadening of a line. The effect is shown in Fig 1A. The original line is shown at *a* and partial absorption of the central radiations results successively in *b* and then in *c*. Fig 1B shows that

when the central absorption becomes more pronounced a spurious doublet is the result, and care must be taken to avoid this

Stark effect

The broadening produced by thermal agitation is usually not so serious as that due to Stark effect. It was discovered by Stark that a sufficiently intense electric field influences the positions of the electrons so that the terms are split in a manner somewhat analogous to the effect discovered by Zeeman with a magnetic field. The effect of a strong electric field is to split up each line into a group of components, but in the usual sources which are employed for spectroscopic purposes, the fields are such, that the lines are merely broadened. The best way to reduce Stark broadening is by using the Paschen hollow cathode type of discharge, in which the whole discharge is within a conducting cylinder so that the electric fields are negligibly small, except at the circumference of the discharge.

Line width due to collision and pressure

Atoms which are struck by others, either just before or at the instant of emitting radiation, are affected so that the wave-length of the radiation may be increased or decreased. The average result in a vapour is the production of broadened lines, and since the number of impacts increases with the rise in pressure, it is advisable to work with as low a pressure as possible. More important than direct impact is the effect of the inter-atomic electric fields which produce serious Stark broadening.

With suitable precautions lines can be made very sharp, and in order to take full advantage of the sharpness, instruments with very high resolving powers should be used. For a full discussion of the possibilities and ranges of the instruments regularly employed for fine structure observations, the reader is referred elsewhere.¹ For the visible region of the spectrum the silvered Fabry-Perot etalon is most frequently used, and in the ultra-violet region,

quartz Lummer plates and the reflecting echelon are now being regularly employed. The most frequently used sources are the Schüller modification of the Paschen hollow cathode discharge,² cooled arcs, Geissler tube discharges, and high frequency excitation at low pressures.

REFERENCES

¹ W. E. Williams, "Applications of Interferometry" (Methuen, 1930)

² H. Schüller, *Zeit. f. Phys.*, 59, 149, 1930

CHAPTER III

MULTIPLICITY IN LINE SPECTRA

IN order to be able to understand the origin of the fine structures of the spectra, it is necessary to have a clear understanding as to how gross structure multiplets arise. It is not possible to give a comprehensive account here, and for a full treatment the reader is referred elsewhere.¹ The more important general features, in so far as they bear upon the subject of fine structures, will, however, be discussed here. It will be assumed that the reader is familiar with the elementary Bohr theory of the hydrogen atom, and also understands how the Periodic Table has been built up by the process of completion of the electron shells. An excellent introductory account is given in Johnson's "Spectra" in this series.² The simplest type of spectrum, namely that arising from a hydrogen-like atom such as sodium, will first be discussed. Such an atom possesses only one valence electron, the transition movements of which give rise to the optical spectrum. The discussion will then be extended to two electron and later to more complex cases by the help of a vector model. Although the wave mechanics has shown that the vector model is not completely exact, yet it is extremely helpful and valuable as an aid to the solution of gross and fine structure problems and sufficiently correct for our purposes.

One-electron spectra

A convenient example of a hydrogen-like atom is sodium, which consists of a nucleus and eleven outer electrons. In this atom, two inner electron shells, namely the K and L shells are completely filled, and in the third shell there is

one electron, the valence or optical electron. For spectroscopic purposes the first shell is denoted by the number 1, the second by 2, etc. In the vector model of the atom, each electron is considered to be spinning, the mechanical moment of the spin being the same for each electron and equal to $s \cdot \frac{h}{2\pi}$, where $s = \frac{1}{2}$ and h is Planck's constant.³ s is called the spin quantum number of the electron. Since, in addition, an electron rotates in its orbit, it also possesses an orbital angular momentum, and the value of this orbital momentum is $l \cdot \frac{h}{2\pi}$ for each electron, where l is called the orbital quantum number. In contradistinction to the spin, different electrons may possess different l values, they may have any of the values 0, 1, 2, 3, 4, etc.,

TABLE I

l value	0, 1, 2, 3, 4,
Electron designation	s, p, d, f, g,
Atomic state	S, P, D, F, G, .

according to the eccentricity of the orbit in which the electron moves.

In general an electron moves in an elliptical and not in circular path around the nucleus, and orbits of the same energy, but of different eccentricities, are possible for a given electron. *The numerical value of l is a measure of the ellipticity of the orbit*, the smaller the l value, the more eccentric is the path. An orbit of given eccentricity is designated by a letter, the letters corresponding to different l values. The particular letters which are employed are so used because of historical associations. Rows one and two of Table I show the electron designations for various l values.

³ It will be recalled that the first orbit is termed a 1 orbit, the second a 2 orbit, etc., and an electron in any orbit may

have any of the l values. Thus an electron in the first orbit with $l = 0$ is called a $1s$ electron and similarly, for example, an electron in the second orbit with $l = 1$ is designated as a $2p$ electron. Using this notation the complete structure of the *normal* sodium atom, which possesses eleven electrons, is written as $1s^2, 2s^2, 2p^6, 3s$, meaning that there are two $1s$ electrons, two $2s$, six $2p$ and one $3s$ electron in the whole atom. The number of similar or "*equivalent*" electrons, as they are called, is indicated by the index. The optical spectrum is produced by movements of the $3s$ electron, for the inner shells, the first with two and the second with eight electrons, are completely filled, and only contribute to the spectrum in so far as they screen off the nuclear charge from the valence, or optical electron, as it is called.

Spectral terms of a one-electron atom

By "one-electron atom" is meant an atom with one valence electron, such as sodium or caesium. In such an atom only this one valence electron comes into consideration spectroscopically. The electron possesses both a spin and an orbital motion, and being a charged particle, these two angular momenta produce magnetic fields. The spin magnetic field and the orbital magnetic field interact with each other so that in effect the mechanical spin \mathbf{s}^* and the mechanical orbital moment \mathbf{l} combine together to form a resultant by virtue of their magnetic fields. This resultant, called the inner quantum number, is denoted by the letter \mathbf{j} and is obtained by the vectorial addition of \mathbf{l} and \mathbf{s} , that is to say $\mathbf{j} = \mathbf{l} + \mathbf{s}$. Since \mathbf{s} is constant and equal to $\frac{1}{2}$, and as \mathbf{l} varies for different types of orbit, it follows that the inner quantum number also varies for orbits of different eccentricities. The sodium atom in the normal unexcited state has the optical electron in the $3s$ orbit and as seen from Table I the l value for an s orbit is zero, so that

* It is usual to omit the $\frac{h}{2\pi}$ factor since this is always understood. The letters $\mathbf{l}, \mathbf{s}, \mathbf{j}$ represent vectors, and are therefore in heavy type.

values, and when $s = \frac{1}{2}, 1, \frac{3}{2}, 2$, etc., the terms are called doublet, triplet, quartet, quintet, etc., the multiplicity subscripts being 2, 3, 4, 5, respectively.

Consider what happens when the sodium atom is excited so that the optical electron is forced out of its normal $3s$ orbit into the higher $3p$ orbit. Since the electron is now in a p orbit, the l value is 1 (see Table I) and the atom is in a P state. Two values for j are now possible, namely, that in which the electron spin s is parallel with l and that in which it is anti-parallel. There are thus two values of j namely, $j = l \pm s$, i.e. $j = 1 \pm \frac{1}{2}$, so that j may be equal to $\frac{1}{2}$ or $\frac{3}{2}$. It follows that two terms are formed, these being ${}^2P_{1/2}$ and ${}^2P_{3/2}$. The terms are doublet terms, as $s = \frac{1}{2}$ for the single electron concerned, and, as just shown, multiplicity is $2s + 1$. It is easy to see that a $3d$ electron (with $l = 2$) will produce ${}^2D_{3/2}$ and ${}^2D_{5/2}$ terms in a similar manner. Since, say, a ${}^2P_{1/2}$ term may be produced by either a $3p$, $4p$, $5p$, etc., electron, it is customary to specify the terms more completely by writing the designation of the optical electron before the term. For instance, the ${}^2P_{1/2}$ terms produced by $3p$ and $4p$ electrons respectively, are described as $3p\ {}^2P_{1/2}$ and $4p\ {}^2P_{1/2}$. Other examples are, say, $4d\ {}^2D_{3/2}$ and $5f\ {}^2F_{7/2}$, etc. A line transition from a $3p$ to a $3s$ orbit would be written as $3s\ {}^2S_{1/2} - 4p\ {}^2P_{1/2}$ as a particular instance.

Terms in alkali spectra

The terms which arise in alkali spectra are shown in Fig. 2. All the terms other than S terms are double, since two values for j are permitted, whereas for the S terms $2j + 1 = 1$.

In the two components of a doublet term, e.g. $4p\ {}^2P_{1/2}$ and $4p\ {}^2P_{3/2}$ that with the smaller j lies deepest, and *such a spectrum is called a normal spectrum*. In some atoms the terms are completely inverted, the biggest j value lying deepest and there exist regular intermediate stage graduations between normal and inverted spectra.

A group of terms such as $3p\ {}^2P_{1/2}$, $4p\ {}^2P_{1/2}$, $5p\ {}^2P_{1/2}$, etc.,

is called a sequence of terms, and each sequence tends to a common limit which represents the ionisation limit of the atom. When the optical electron is lifted to this limit it does not fall back, but leaves the atom, which is then charged, and is called an ion. The number 3, 4, 5, 6, etc., before the p in the term designation is called the current total quantum number n , and Fig. 2 shows that the intervals

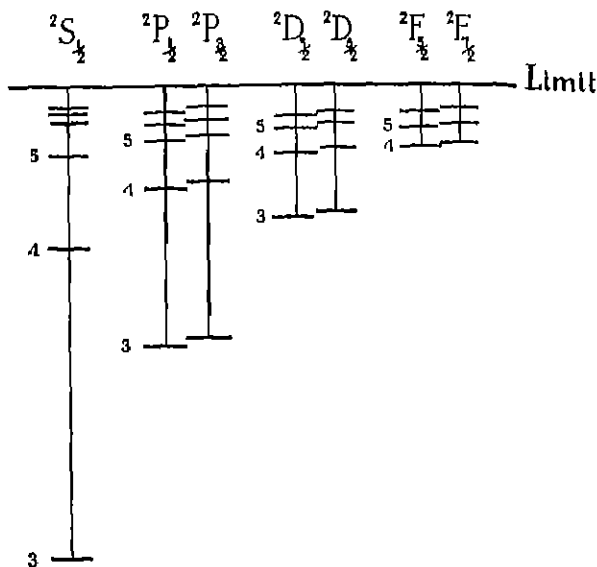


FIG. 2.—The term scheme of sodium and the alkali-like atoms.

between the components of a doublet term steadily diminish as n , the number of the orbit the optical electron occupies, increases.

When the electron is excited and lifted up to a high orbit, it tends to fall back to a lower orbit. Not all transitions are possible, and amongst those which do occur some are more probable than others. Transitions are limited by a selection principle which states that l must change by ± 1 .

and j by ± 1 or 0, the transition $\Delta j = 0 \rightarrow 0$ being excluded. Under special conditions of excitation these rules may be violated, but such departures need not concern us at present.

As $\Delta l = \pm 1$, transitions from S to P or P to D (or vice versa) are allowed, but an S to D transition is, for example, forbidden. All the transitions, from, say, a given

2P to a given 2D state, that are allowed by the j selection principle, together form a *multiplet*, and the multiplet is named according to the multiplicity of the terms involved, i.e. in this case it is called a doublet multiplet. A typical doublet multiplet is illustrated in Fig. 3, which shows how a 2P - 2D multiplet arises. Some transitions are more probable than others, resulting in lines of differing intensity, and in the illustration the heights of the lines are drawn proportional to the line intensities.

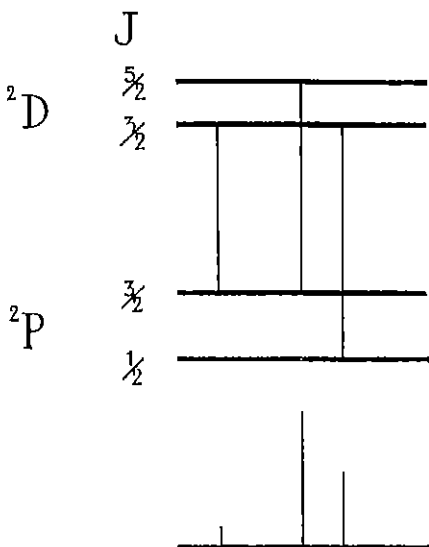


FIG. 3—A typical doublet multiplet, note that three lines are produced but the doublet name is derived from the term multiplicity.

the heights of the lines are drawn proportional to the line intensities. The intensities of the components of a multiplet obey laws which are very similar to those obeyed by fine structures, and since the latter have to be considered in detail, it will be sufficient to state the "sum rule" which governs the relative intensities of the components of a given multiplet. Simply stated, the rule

is that the sum of the intensities of all the lines coming to any given j level is proportional to $2j + 1$. It is to be noted that a doublet multiplet can consist of more than two lines, the doublet appellation refers to the *multiplicity* of the terms and not to the *number* of lines in the multiplet patterns.

Two-electron spectra Electron couplings

Having examined the alkali-like spectra, the next step is to discuss the spectra produced by atoms which have two valence electrons, e.g. Ca or Hg, etc. The two valence electrons interact with each other, and as the principles employed here are fundamentally the same as those for more complex electron systems, they will be discussed in detail. As in the previous case considered, each of the two valence electrons possesses a spin angular momentum $s = \frac{1}{2}$, and an orbital angular momentum l which may have any of the values 1, 2, 3, 4, 5, etc. There are, therefore, four vectors to take into consideration, and these may combine in different ways to form a resultant J which will represent the total angular momentum of the atom. (*In the vector notation small letters are used to represent specific angular momenta for individual electrons, and capital letters for resultant sums*). The vectors may combine in a variety of ways and one may distinguish two extreme types of coupling called LS* and jj respectively.

LS Coupling

There are four vectors which will couple in a two electron atom, namely, s_1 and s_2 , the two electron spins, and l_1 and l_2 , the two orbital angular momenta. In LS coupling, the binding between the spins s_1 and s_2 is so strong that these form a resultant spin S . Correspondingly, the binding between the two orbital angular momenta l_1 and l_2 is very strong and these add up to form a resultant orbital angular momentum L . It means, therefore, that the link-

* This type is often termed Russell-Saunders coupling after its discoverers.

age of the mutual spins is so strong that it is not influenced by the orbital angular momenta, at the same time, the linkage of the orbital angular momenta is so strong that the electron spins cannot affect it. There are now two resultant vectors S and L and these in turn couple to form a resultant J . As in the simple alkali case, the multiplicity is now $2S + 1$ *. Furthermore the term type is determined by the numerical value of the resultant L , i.e. for $L = 0, 1, 2, 3, 4, 5$, etc., the terms are S, P, D, F, G, H , etc. *It is important to notice that the term letter notation is not the same in capitals as the letter notation of the optical electron in small letters*, as was the case with hydrogen-like spectra. The selection rules now become

$$\Delta J = \pm 1 \text{ or } 0 \text{ [} 0 \rightarrow 0 \text{ excluded]}$$

$$\Delta L = \pm 1$$

jj coupling

Whereas in LS coupling all the spins unite to form a resultant spin S , and all the orbital momenta form a resultant L , the case called jj coupling is very different. The same four vectors s_1, s_2, l_1, l_2 are under consideration, but the mode of combination is altered. Here the coupling between the s_1 and l_1 of the one electron is so strong that it forms a resultant j_1 . Similarly the spin and orbital momenta s_2, l_2 of the other valence electron form a resultant j_2 . The other possible influences are not sufficient to break these pairings so that the two resultants j_1 and j_2 now couple to form a resultant J . Summarising then, in LS coupling all the l values form a resultant L and the s values a resultant S which then combine to form J , whilst in jj coupling the l and s of each electron combine to a resultant j for each electron, and then all the j values add up to form J .

Regular intermediate stages exist between LS and jj couplings and these are conveniently shown below †

* s has always the value $\frac{1}{2}$, but S , being a resultant, may have other and larger values.

† See Pauling and Goudsmit, "Structure of Line Spectra" (1931)

$$\{(l_1 l_2)(s_1 s_2)\} = \{LS\} = J \quad (1)$$

$$\{(s_1 l_1)(s_2 l_2)\} = \{j_1 j_2\} = J \quad (2)$$

$$[(s_1 l_1) s_2] l_2 = [(j_1 s_2) l_2] = J \quad (3)$$

$$[(s_1 l_1) l_2] s_2 = [(j_1 l_2) s_2] = J \quad (4)$$

Two vectors within a bracket are directly coupled together. The first and second cases are the LS and jj types already mentioned. In case (1), $l_1 l_2$ couple to L and $s_1 s_2$ to S, finally L and S give J. In case (2), $s_1 l_1$ form j_1 and $s_2 l_2$ form j_2 , finally j_1 and j_2 give J.

In the third case $s_1 l_1$ give a resultant j_1 which breaks up the link between $s_2 l_2$ and first combines with s_2 . The vector pair $j_1 s_2$ then combines with l_2 to give J. The fourth case is similar, except that j_1 first binds itself with l_2 instead of s_2 .

It can be shown that no matter what manner of coupling may exist, the *number* and *type* of the terms which are produced by the vector combinations remain the same, this has considerably simplified analysis. The multiplicity has been defined as $2S + 1$, but since it is only in pure LS coupling that a resultant S exists, the multiplicity for JJ or intermediate stage coupling has, in this sense, no real meaning. As, however, the number and type of terms are independent of the nature of the coupling, it is convenient to use the same notation, for the multiplicity gives the number of terms, independent of the existence of S. The greater number of actual spectra hitherto analysed are cases of the LS type of coupling, which will be illustrated by an example.

Graphical representation of coupling processes.

As a typical example of a two-electron spectrum of the normal type, calcium will be considered. In the normal state calcium has two valence electrons, both of which are in 4s orbits and either of these may be excited, either separately or simultaneously. Let us first consider the case when only one of the valence electrons is excited, the other remaining permanently in its 4s orbit. The optical electron may go either into a ns, np, nd, etc., orbit according

to the excitation energy imposed upon it, and the two electrons with their different energies interact to give a resultant J . In calcium, the coupling is LS in type, meaning that the electron spins unite to a resultant S and the orbital momenta to a resultant L . Two distinct classes of terms arise, those in which the two electron spins s_1 and s_2 oppose, giving a resultant $S = 0$, and those in which s_1 and s_2 add to form a resultant $S = 1$. The first group is a singlet group, the second a triplet (multiplicity $= 2S + 1$). The optical electron may have varying L values so that a set of singlet and a set of triplet terms arise.

The *singlet* set of terms are quite simply formed. The normal state of the atom is that in which both electrons are in $4s$ orbits, and therefore each has $l_1 = l_2 = 0$. In the singlet system $S = 0$ and as the resultant L also equals zero, it follows that $J = L + S = 0$ so that the deepest term of the spectrum, i.e. the *normal* term, is 1S_0 or, more accurately described, $4s^2 \ ^1S_0$. When the optical electron moves to $5s$, $6s$, etc., the terms formed are $4s \ 5s \ ^1S_0$, $4s \ 6s \ ^1S_0$, etc., so that a sequence of 1S_0 terms is produced. Instead of going into an s orbit, the optical electron may be lifted into a p orbit, for which $L = 1$. As before, the resultant S still equals zero, but the resultant orbital momentum L is equal to $l_1 + l_2 = 1$. The term therefore is a 1P term and as $J = L + S$ it is a 1P_1 term. Similarly when the optical electron is lifted to a d orbit, a 1D_2 term is formed, etc.

In order to see how *triplet* terms arise, a vectorial graphical representation proves useful. The triplet system is that in which the two electron spins s_1 and s_2 act parallel so as to produce a resultant $S = 1$. Owing to the Pauli exclusion principle, it is impossible to have two electrons in $4s$ orbits with their spins parallel, for the Pauli principle states that no two electrons can exist together in the same atom if their n , l , j and m values are the same (m is the magnetic quantum number which exists when the atom is in a magnetic field). This principle, therefore, excludes the possibility of having two $4s$ electrons with their spins parallel. The first allowed state is that in which, as before,

s_2 have formed a resultant $S = 1$, and similarly $l_1 + l_2 = 1$. From this it is seen that J can have any of the three values 0, 1, 2, and the terms 3P_0 , 3P_1 , 3P_2 are produced. From the graphical point of view, it is very useful if we start from the $^2S_{1/2}$ ion term. That is to say, consider the atom ionised, in which state the optical electron is completely removed, leaving the other valence electron in the $4s$ orbit.

The ionised atom will now be in a state identical with the normal state of the one-electron type of atom, i.e. in a $^2S_{1/2}$ state. Now, to produce a Ca I atom with one electron in a p orbit all that is necessary is to add the vector representing the p electron to the vector representing the $^2S_{1/2}$ state of the Ca II atom. This is shown in Fig. 4. The left, A, shows the $^2S_{1/2}$ ionic term of Ca II in which the only existing vector is the electron spin, $s_1 = \frac{1}{2}$, of the $4s$ electron. This is shown vectorially by a thick hollow arrow in the vector picture at the right of the term. The direction of the resultant J is shown by means of a dotted arrow, and of necessity coincides with the direction of s_1 in the $^2S_{1/2}$ term. The effect of adding a $4p$ electron to the $4s$ electron is shown vectorially at B. The orbital angular momentum ($l_2 = 1$) of the $4p$ electron is shown by the long thin black arrow, and its spin ($s_2 = \frac{1}{2}$) by means of a short thick black arrow. [The reason for distinguishing between the spins of the $4s$ and $4p$ electrons, although both equal $\frac{1}{2}$, will appear later.] The four terms which result from the singlet and triplet combinations of $4s$ and $4p$ are numbered at the right. The first term is the 1P_1 term previously discussed. In the second term all the vectors act parallel, and so produce a 3P_2 term. The third term shows how both the spins couple to a resultant $S = 1$, which then combines at an angle with $L = 1$ to give a resultant $J = 1$. In the fourth term the two spins still act parallel, but their resultant opposes L and so a 3P_0 term is produced.

A schematic diagram of the more important terms obtained in Ca I when one of the valence electrons remains in the $4s$ orbit and the other moves successively to s , p , d , f , g , etc., orbits is shown in Fig. 5. As in the hydrogen-like spectra, all these terms tend to a limit, which is the

normal state in which the ion is left, in this case a $4s\ ^2S_{1/2}$ state. *It is very convenient to imagine all the terms of an atom as being built up by the addition of an electron vector to the terms of the ion.* For example, the addition of a $5s$ electron to the $4s\ ^2S_{1/2}$ state of Ca II produces the 1S_0 and 3S_1 terms of Ca I, and, as shown graphically, a $4p$ electron produces 1P_1 and $^3P_0, ^3P_1, ^3P_2$ terms. The addition of d, f, g electrons can be made in a similar way.

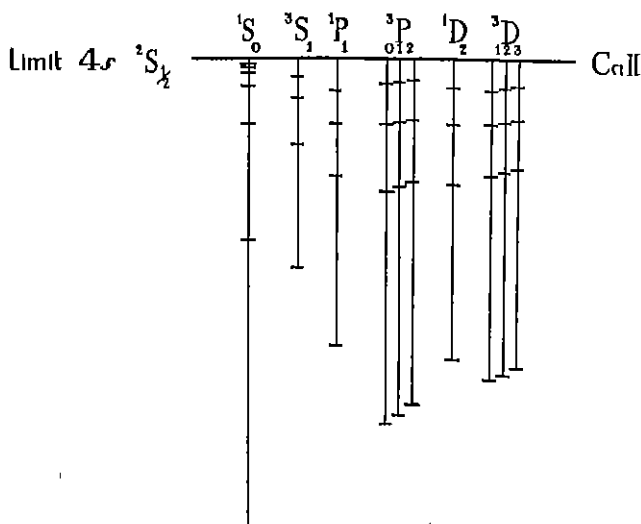


FIG. 5.—Part of the term scheme of Ca I built upon the $4s\ ^2S_{1/2}$ series limit

Series limits

It has so far been assumed that only one of the valence electrons has moved into a higher orbit, but it is possible for both to be displaced when excitation of the atom takes place. For example, the $3d$ orbit is higher than the $4s$ and one electron may be lifted up into this orbit and remain there, whilst the other may be lifted either to an

s, p, d, f , etc., orbit. Or else the first electron is lifted to $4p$ and the second to some other orbit. In each case the terms will tend to different limits, since the ion is left in a different state. Thus, in the first case previously discussed, where one electron was permanently in a $4s$ orbit, the calcium ion is left in a $4s\ ^2S_{1/2}$ state when the optical electron is completely removed. In the second case

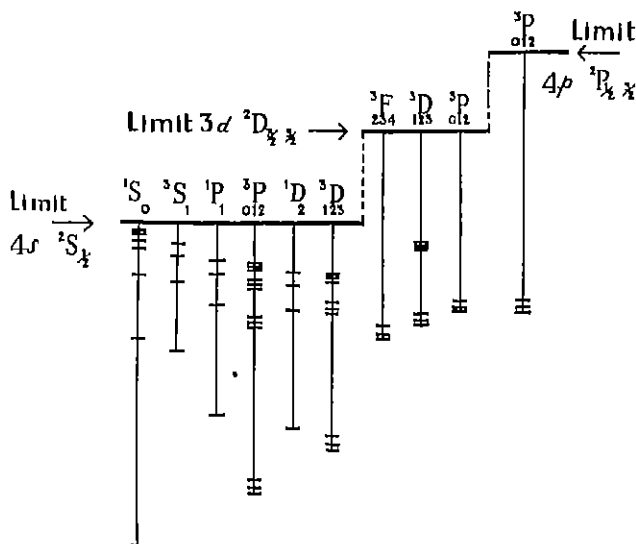


FIG. 6—The main terms and series limits in the spectrum of Ca I.

mentioned above, the electron of the ion is left in a $3d$ orbit when the optical electron is removed, so that the ion may be left either in a $3d\ ^2D_{3/2}$ or a $3d\ ^2D_{5/2}$ state. It follows that all the terms of the calcium atom, which arise when one electron remains in a $3d$ orbit and the other moves to other orbits, tend to two limits, namely $^2D_{3/2}$ and $^2D_{5/2}$. These two terms lie close together, being members of a doublet group, but are both far away from the

$^2S_{1/2}$ state which was the single limit reached by all the terms when only one electron was excited. In an identical manner the terms produced when one electron is in the $4p$ orbit and the other is in some other orbit tend to the limits $4p\ ^2P_{1/2}$ and $4p\ ^2P_{3/2}$, which again lie close together but are both far removed from the 3D terms of the previous case. The limits reached by the terms of Ca I are shown in Fig. 6 and are seen to be widely separated.

In order to be able to build up term schemes correctly, it is important to know exactly what the series limits will be, and to which particular limit a given sequence of terms will converge. It will be seen later that this has a very important bearing upon the problem of fine structures, and for this reason series limits have been discussed here. Complete tables of series limits have been investigated by Hund⁴ and the reader is referred to Hund's work for particular cases. Hund⁵ has given two sets of limits, one set being those to which normal terms tend, the other for inverted terms. An example of the application of the rules will be given later when series limits are applied to fine structures.

Equivalent electrons

The Pauli exclusion principle strictly limits the number of electrons with the same n and l value in any atom. In a given orbit there cannot be more than a fixed number of, say, p or d or f electrons. Such electrons are called equivalent electrons. As an example of an atom which has many equivalent valence electrons, the bromine atom may be cited. In the normal state it has seven valence electrons, two of which are in $4s$ orbits and five in $4p$ orbits. The configuration is called a $4s^2.4p^5$ electron configuration, using the notation already described. The two $4s$ electrons are equivalent, and the five $4p$ electrons are also equivalent. The $4s^2$ group is called a closed group, and takes practically no part in producing the spectrum, so that for present purposes it may be neglected, and only the $4p^5$ group need be considered. The spectral terms of the atom are pro-

duced by one of these electrons moving into various orbits. In the normal state the five $4p$ electrons are arranged so that the resultant $S = \frac{1}{2}$ and the resultant $L = 1$. This means that 3P terms are formed and these are the deepest lying terms, the $^2P_{1/2}$ term being deeper as the multiplets are inverted. The remaining important terms of the spectrum are produced by the moving optical electron.

The first group of terms arises when one of the $4p$ electrons is lifted up to the $5s$ orbit, so that the configuration becomes $4s^2 4p^4 5s$. Another group is formed if the optical electron goes instead into a $5p$ orbit, producing a $4s^2 4p^4 5p$ configuration, and so on. Each separate electron configuration forms a number of terms and these can all be conveniently built up by treating the $4s^2 4p^4$

TABLE II

Basic Terms of the Ion Br II	3P	1D	1S
1-electron Configuration			
$4s^2 4p^5$	3P		
$4s^2 4p^4 5s$	3P 4P	3D	1S
$4s^2 4p^4 5p$	$^3(SPD)$ $^4(SPD)$	$^1(PDF)$	3P
$4s^2 4p^4 4d$	$^3(PDF)$ $^4(PDF)$	$^1(SPDFG)$	3D
etc			

electron group as a core to which the optical electron is added in the $5s$, $5p$, etc., orbits. It is seen that the process is not very different from that involved in building up the two-electron spectra, for in the latter, two electrons were coupled together, and at present one electron is to be coupled to a core.

The series limits must be known before any attempt to build up the terms can be made. All the terms of the bromine atom can be predicted by means of Hund's theory, and the most important of these are shown in Table II.⁶

In Table II the electron configurations are shown in the first column and each configuration produces the group of terms shown in the remaining columns. It is usual to distinguish between two classes of terms called odd and even

terms. Odd terms are those in which the sum of the l values of the individual electrons of the term configuration is odd and even terms those in which the sum is even. For

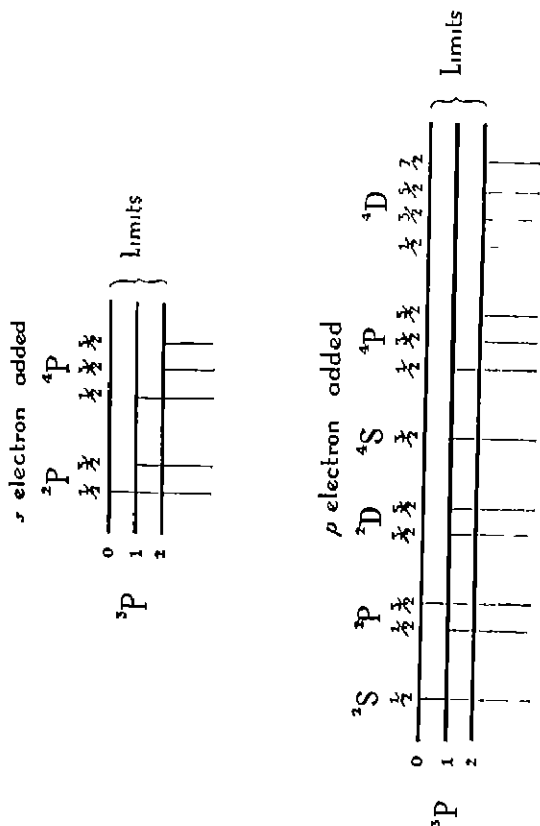


FIG. 7—Series limits of important terms of the Br I spectrum.

example, in the previously considered case of Ca a $4p^2$ term is even and a $4p\ 4d$ term is odd. In Br I $4s^2\ 4p^5$ terms are odd, $4s^2\ 4p^4\ 5s$ even, etc. Transitions may only take

place between odd and even terms. These terms are sometimes distinguished by superscripts, but since the electron configurations are always given here, superscripts are unnecessary. As Table II shows, transitions such as $P \rightarrow P$ or $P \rightarrow F$ are possible providing they are odd-even transitions. In addition to this L restriction, transitions can only take place when $\Delta J = \pm 1$ or 0 (0 \rightarrow 0 excluded).

In Table II the basic ion terms of Br II, are shown in heavy type. These are produced by the configuration of the ion Br I and are the basic terms which produce the terms of Br I when the optical electron is added. They are also the series limits, that is, the limits to which the Br I terms converge. In order to avoid making the table too cumbersome two abbreviations are used. Firstly, a term written as 3P or 4P means the whole sequence of allowable J values, in these cases, 3P_0 , 3P_1 , 3P_2 and $^4P_{1/2}$, $^4P_{3/2}$, $^4P_{5/2}$ respectively. Secondly, a group of terms 2S , 2P and 2D is written $^2(SPD)$ and similarly for other multiplicities. Each horizontal row shows the terms which arise from a given configuration, and the limits to which these terms tend is indicated by the column in which the terms are found.

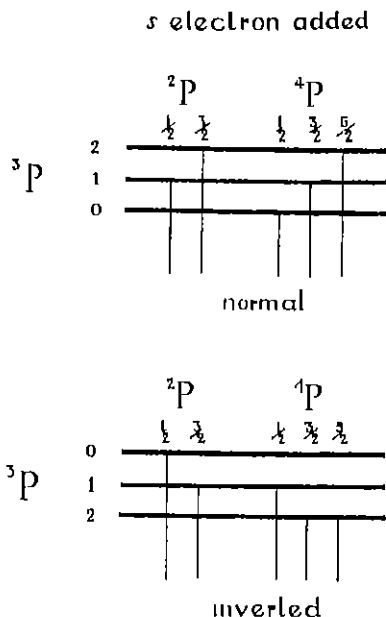


FIG 8 — Showing the difference between the series limits in normal and inverted spectra

The question of series limits is of importance, and since the limits for normal and inverted spectra are different, care must be taken to use the correct limits. The terms in Br I. are inverted, a pictorial diagram of the limits is given in Fig 7. The terms of Br II are also inverted and this appears in the diagram. The diagram illustrates two cases only, namely the important $4s^2 4p^4 5s$ and $4s^2 4p^4 5p$ terms which tend to the 3P limit. The limiting 3P terms are shown by the thick horizontal lines and form an inverted multiplet (the drawings are schematic and not to scale) as shown by the J values on the left. The effect of adding the $5s$ electron is shown at (a) by the vertical lines which indicate to which limit each term sequence tends. For instance, $^2P_{1/2}$ tends to the limit 3P_0 whilst $^4P_{1/2}$ tends to 3P_1 . Conversely the $^2P_{1/2}$ term of Br I. is formed when the $5s$ electron is added to the 3P_0 term of Br II, and the $^4P_{1/2}$ term of Br I is formed by adding the electron to the 3P_1 term of Br II. The method by which this is obtained will be shown later by means of a vector diagram. Fig 7(b) shows the effect of adding a $5p$ electron to the ion terms, giving in fact the terms and limits of the $4s^2 4p^4 5p$ configuration. For comparison purposes Fig 8 shows how the series limits for normal and inverted multiplets are entirely different, although similar multiplets are considered.

Vector coupling in bromine

The vector coupling in bromine is somewhat similar to that of a two-electron spectrum and is shown for the $4s^2 4p^4 5s$ configuration in Fig. 9. In effect, the optical electron $5s$ is to be coupled vectorially to the core $4s^2 4p^4$. The core produces the 3P_0 , 3P_1 , 3P_2 inverted multiplet terms shown at A, which are the series limits, so that the core is equivalent to a vector with $L = 1$ and $S = 1$, for only such resultants will give a 3P multiplet*. The

* In order to avoid complication it is assumed that strict LS coupling takes place. This is not true for bromine, but as it has only been chosen as an example because of its many valence electrons, the contradiction is of no consequence here.

vector diagrams for the 3P basic ion terms of Br II are shown to the right of the terms A. The long thin black

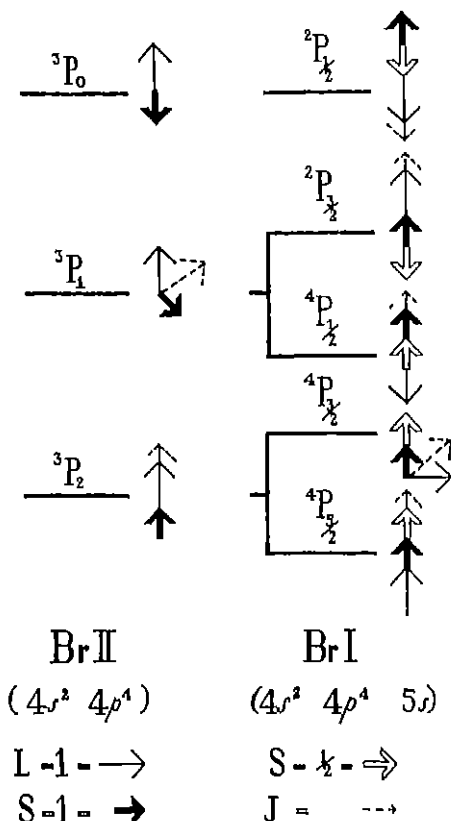


FIG. 9.—Vector coupling diagram showing how the 3P and 4P multiplet terms of the $4s^2 4p^4 5s$ configuration of Br I arise

arrow gives the resultant $L = 1$ and the short thick black arrow the resultant $S = 1$ (compare Fig. 4). As the terms

are inverted, the largest J value (2) lies deepest. As before, the direction of J is shown by the dotted arrow.

The result of coupling the $5s$ electron to the core is shown at B and this should be studied carefully. The electron is added in LS coupling which means that *the original coupling of the L and the S can be broken, but the individual ll couplings and ss couplings remain intact*. The new s value of the added electron may combine either parallel or anti-parallel with the already existing S value of the core, to form a new resultant S . The same is true for L (in this case the l of the added electron happens to be zero). The new L and S values then combine in the usual manner to give J . The $5s$ electron is shown by means of a short thick hollow arrow and *is always added in the same direction (either positively or negatively) as the original S value of the core*.

In the two higher lying Br I terms, the spins oppose, so that the resultant spin quantum number is $\frac{1}{2}$, producing an inverted 3P doublet. In the three deeper terms the resultant spin of the core acts parallel to that of the $5s$ electron, so that the terms are 4P ($S = \frac{3}{2}$ and multiplicity $= 2S + 1$) and are also inverted.

The vector method just described can be used for all configurations if the terms predicted by Hund's theory are taken as a guide and the correct series limits used.

Interval rule.

In most of the diagrams previously given, the exact number and description of the terms of a multiplet has been given, but little attention has been paid to the relative positions of the terms such, for example, as the relative spacings between the terms of 3P group. In a normal triplet, the terms lie in the order 3P_0 , 3P_1 , 3P_2 , the term with the smallest J value lying deepest. The interval between the first pair of terms is different from that of the second pair, because the interaction energy between the spins and angular orbital momenta differs for the various terms, and the position of a term depends upon this interaction energy.

It can be shown that, in LS coupling, the interaction energy between the resultant spin S and the resultant angular orbital momentum L is given by E , where

$$E = A' SL \cos(SL),$$

A' being called the interval factor for a reason which will appear later. The interaction energy between two vectors is proportional to the cosine of the angle between those vectors, and it can be shown that the above expression is equivalent to

$$E = \frac{A'}{2} \{J(J+1) - L(L+1) - S(S+1)\}$$

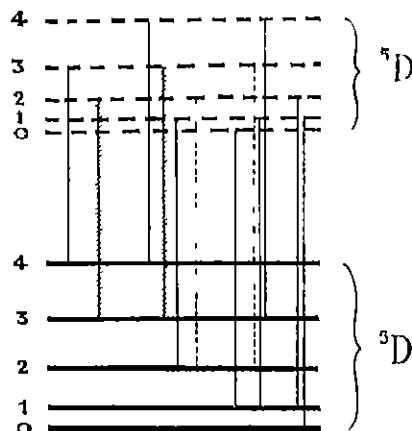
This formula expresses what is known as the Landé Interval Rule, after its discoverer, and from it the ratio of the intervals in a multiplet can be calculated.

Since the position of a term is given by its interaction energy, the difference of energy between two terms will be proportional to their separations and the formula shows that for a multiplet group arising from a given S and L , the energy differences of the different terms are proportional to the differences of the $J(J+1)$ values. With a 4D multiplet group, for example, $S = \frac{3}{2}$ and $L = 2$, giving four terms with the J values $\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. According to the Landé rule the successive energy differences between adjacent pairs of terms, being proportional to $J(J+1)$, are in the ratio

$$\left\{\frac{7}{2} \cdot \frac{9}{2} - \frac{5}{2} \cdot \frac{7}{2}\right\} \left\{\frac{5}{2} \cdot \frac{7}{2} - \frac{3}{2} \cdot \frac{5}{2}\right\} \left\{\frac{3}{2} \cdot \frac{5}{2} - \frac{1}{2} \cdot \frac{3}{2}\right\},$$

that is, in the ratio 7 : 5 : 3, or that the ratios of the intervals of the terms of the multiplet are the same. It will be seen that these ratios are given directly by the ratios of the different J values when the smallest J value is neglected. This simplified form of the Landé rule is true for all cases in which strict LS coupling takes place. It is both true for normal and for completely inverted multiplets, but it will be obvious that when a multiplet is partially inverted the rule completely fails. Whilst the ratio of the intervals between the terms is a function of J , their actual separations depend upon the value of the interval factor A' . This is

determined by the distance of the electrons from the nucleus, the degree of penetration of the orbits, the screening effect of other electrons, and the interaction energy between the electrons themselves. The interval factor, therefore, differs for different multiplets, usually diminishing as the n of the optical electron increases. For this reason



the separations in, say, the $4s\ 4p\ ^3P$ multiplet of $Cu\ I$ are greater than those in the $4s\ 5p\ ^3P$ multiplet, although the ratios of the intervals are the same in both cases (in effect, the difference is merely one of scale).

An example of the line pattern formed by the transitions between two multiplet terms is shown in Fig 10, the case illustrated being that of transitions between two 5D multiplet term groups. The interval factor of the upper set of terms is made less than that of the



FIG. 10—A typical $^5D - ^5D$ multiplet pattern.

lower, but the interval rule is obeyed by both. The intensities of the lines differ according to the intensity rule on page 16. The resulting line pattern is complex because of the different interval factors and the varying intensities.

The line pattern of a multiplet.

The line pattern of a multiplet can vary in width from a fraction of a wave number to several thousand wave numbers, and various methods have been used to assist in sorting out members of a multiplet from a large group of lines. *The most important way is the method of constant frequency differences* which can be seen from Fig 10. An examination of the transitions shows that the two hatched lines *ab* have the same frequency difference as the two dotted lines *cd*, namely the interval between the upper terms with $J = 3$ and $J = 2$ respectively. It follows that a search among the lines suspected to belong to the multiplet will reveal this common difference, even when other foreign lines are present. It will be observed that a large number of common differences exist, and from these the multiplet can generally be built up, due regard being paid to the intensities which should obey the intensity law. There are, of course, many multiplets in which the intensity or interval rules break down and other means must be used to assist in analysis, such as Zeeman effect observations.

For further study in multiplet analysis the reader is referred to Hund's "Linienpektren."

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CHAPTER IV

THE EFFECT OF A NUCLEAR SPIN

Nuclear spin.

Two types of fine structure occur in line spectra, and these arise from entirely different causes. One type, called the isotope fine structure, is due to the fact that many elements are not simple but consist of a number of isotopes. Since the separate isotopes of an element have identical extra-nuclear electron configurations, the spectra emitted by each of these are almost the same, and the lines of the one isotope practically coincide with the lines of the other. There is, however, in some cases, a measurable displacement for certain lines, the displacement being due either to the different masses or varying electrical properties of the different isotopic nuclei or else to the motion of the nucleus. In favourable cases these displacements can be observed as a fine structure effect. This will be discussed in a later chapter.

The second type of fine structure is due to the fact that the nuclei of certain atoms have the property of a spin. It was first suggested by Pauli¹ that fine structures (excluding isotopic effect) could be accounted for if it were assumed that the nucleus possessed a magnetic moment which perturbed the motions of the external electrons. This nuclear magnetic moment would couple vectorially with the magnetic moment of the valence electrons and behave as if a new type of quantum number had been introduced. If the nuclear and the electron magnetic moments couple in accordance with the usual vector rules, it follows that each electron term would be divided into a group of terms,

the energies varying between the two limits formed when the nuclear moment is parallel and anti-parallel to the electron moment. In between these limiting terms further energy states may occur, the number depending on the quantum values of the respective moments. The expression "level" will be retained to describe any of these fine structure energy levels and the word "term" confined to denote the gross structure energy state.

Associated with the magnetic moment is a mechanical moment, which being quantised, becomes some multiple of $\frac{h}{2\pi}$. The mechanical moment is usually denoted by $I\frac{h}{2\pi}$ and the coefficient I is termed the nuclear spin. The existence of a nuclear spin had already been previously inferred, for the nuclei of certain atoms, from the study of band spectra. The investigation of the band spectra of hydrogen showed definitely that each of the protons, which are the nuclei of the hydrogen atoms forming the hydrogen molecule, possesses a spin with $I = \frac{1}{2}$, i.e. the mechanical moment of the spinning proton is $\frac{1}{2}\frac{h}{2\pi}$, the same as in the case of the spinning electron. The ratio of the magnetic moment of the proton to that of the electron should be approximately in the inverse ratio of the two masses so that the magnetic moment of the proton should be about $\frac{1}{1836}$ that of the electron*. This explains the minuteness of the scale of fine structures, in comparison with that of the ordinary gross structure multiplet. If we ignore the special case of nitrogen, a study of the intensities of the band spectra of homogeneous molecules seems to point to the rule that the nuclear spin of light even atomic weight elements is zero, while the odd elements have half integral spin values². It can be shown that if the identical nuclei of the two atoms forming a homogeneous dipolar molecule have a nuclear spin I , the alternate lines in the rotational structure of the band spectrum have an intensity ratio

* Actually it is 2.5 times greater than the value expected on the simple theory (p. 107)

$\frac{I+1}{I}$ When $I = 0$, the ratio becomes infinite, so that alternate lines are absent. This occurs in the spectra of He_2 , C_2 , O_2 and S_2 .

Nuclear spins are usually found to be half integral and vary in value from $\frac{1}{2}$ to $\frac{9}{2}$. Some recent experimental evidence suggests possibly higher values such as $\frac{11}{2}$, but this remains to be confirmed. A detailed discussion will be given later of nuclear building-up processes with reference to the experimental values of the spins. Only two atoms, N^{14} and H^2 , have integral values, the spin being 1 in both cases.

Interaction of nuclear and electron magnetic moments

As we have shown in the previous chapter the nett resultant moment of the electron system of an atom is given by J , so that if the atom possesses a nuclear spin I it is to be expected that the two vectors I and J should combine vectorially to form a resultant quantum number. This is termed the *fine structure quantum number*, and is denoted by the letter F , which is a vector quantity, giving the total angular momentum of the whole atom. We find that I and J can combine vectorially to give a number of values so that each term of the spectrum (henceforth called the gross structure term) will divide into a tiny multiplet group of fine structure terms, which for purposes of differentiation will be referred to as *levels*. The values that F can have are given by the vectorial relation $F = I + J$, so that by analogy with the case of multiplets discussed on page 12 it will be seen that if J is larger than I the total number of combinations possible is $2I + 1$, hence the gross structure term divides into $2I + 1$ fine structure levels. If, on the other hand, J is less than I the number of arrangements which is possible is $2J + 1$. Since many terms split up in this manner, a gross structure line will have the line structure of a multiplet on a minute scale, and general considerations show that a selection principle will operate in the production of this fine structure multiplet. The

predicted and observed selection principle is that $\Delta F = \pm 1$ or 0 (0 \rightarrow 0 being excluded), and hitherto no exceptions to this rule have been found

The interaction energy between the two vectors \mathbf{I} and \mathbf{J} is dependent upon a number of different factors. Firstly, it depends upon the actual value of the magnetic moment of the nucleus as distinct from its mechanical moment, for it is primarily the magnetic fields which have to couple. It is, of course, true that the magnetic fields can only arise because the charged particles in motion have mechanical moments, but since the coupling between the mechanical moments occurs through magnetic linkage, it is the value of the magnetic moment that determines the interaction energy of \mathbf{I} and \mathbf{J} . The nuclear magnetic moment is usually written as μ , where $\mu = I g(I)$, so that $g(I)$ is the ratio of the magnetic to the mechanical moment when quantum units are employed. $g(I)$ is a pure number, and as its value is determined by the internal structure of the nucleus, it may be very small at times. A second factor affecting the interaction energy is the nuclear charge, for the higher the degree of ionisation the greater is the coupling energy between the extra-nuclear electron moment \mathbf{J} and the nuclear spin \mathbf{I} . A third factor which is extremely important depends upon the eccentricity of the orbit of the optical electron. If the orbit is very eccentric, a high degree of penetration of the inner shells takes place and the optical electron approaches very closely to the nucleus so that the coupling becomes very strong. It will be at once apparent that the coupling energy of an s electron will generally be much greater than that of a p electron, etc.

Let us consider a one-electron system, it is convenient to imagine the coupling between \mathbf{I} and \mathbf{J} as consisting of two parts. \mathbf{I} couples with the orbital angular moment of the electron, that is, IL coupling takes place, and \mathbf{I} couples with the electron spin so that IS coupling also occurs. When these two effects are added the nett interaction energy between nucleus and electron is obtained.⁸ The

final result shows that the energy W is given by the following expression¹

$$W = A J(J+1) \cos(\mathbf{IJ})$$

which can be reduced to the form

$$W = \frac{A}{2} [F(F+1) - J(J+1) - L(L+1)]$$

Comparing this with the formula for ordinary multiplets (see page 31) it will be seen that the two formulæ are identical if J, L and S are replaced by F, J and I . Since this is identical in form with the formula for gross structure multiplets, it follows that the energies of the fine structure levels are also given by the Landé interval rule. The interval between the fine structure multiplet A can be approximated for the simple case of one electron and it is found that A is proportional to

$$g(I) \frac{Z_i z^2}{n^3 L(L+\frac{1}{2})(L+\frac{1}{2})},$$

where Z_i and z are respectively the effective charge of the nucleus in the inner and outer portions of the penetrating orbit, and n is the effective Rydberg number. This formula includes the conditions referred to concerning the value of the nuclear moment, the nuclear charge and the degree of penetration. Calculation shows that the interval for the gross structure multiplet, A' of a one-electron atom

differs from the above value A by the factor

this it follows that the ratios of the scales of fine structure for gross structure multiplets should be given

by $\frac{g(I)}{Z_i}$, but the formula is only very approximate and the agreement with experimental results is only partial.

The formulæ for the fine structure intervals have only been developed for a few electron systems though the general theory is very incomplete.

important facts have already been deduced and experimentally verified. As previously stated the actual width of a structure in a term, that is to say, the total spread of the fine structure multiplets, depends upon the coupling between \mathbf{I} and \mathbf{J} . This, in turn, depends upon the closeness of approach of the optical electron to the nucleus. The more elliptic the orbit, the more likely will the electron penetrate the inner shells. It will not only approach the nucleus more closely, but, when it penetrates closed electron shells, the screening effect of these shells will be reduced. This is equivalent to a considerable increase in the effective nuclear charge which further increases the tightness of the coupling, as it is called. Since the smaller the l value of an orbit, the more eccentric is its shape, it will be expected that elections in s orbits will produce much wider structure than electrons in p orbits, etc. Correspondingly, the width of a $4s$ electron term should be greater than that of a $5s$ electron. Special attention may be directed to the case of p orbits. There are two distinct kinds, depending upon whether the electron spin assists or opposes the orbital angular momentum. In particular, in jj coupling the p electron can have j values $\frac{1}{2}$ or $\frac{3}{2}$ [for $l = 1$ and $s = \frac{1}{2}$]. These different orbits are designated as $p_{1/2}$ and $p_{3/2}$, respectively. The $p_{1/2}$ electron is in the more elliptical and more penetrating orbit and should produce wider fine structures than the $p_{3/2}$ electron. This has been verified experimentally.

Fine structure in one-electron spectra

The vector model previously employed to illustrate gross structure multiplets can also be applied to study fine structure multiplets.

The first new consideration is the question of the actual numerical value of the nuclear spin, a fact which introduces a complication. For example, two atoms may give spectra in which the gross structure multiplets are identical, except that their scales differ, but if the atoms have different nuclear spins, the fine structures of the two spectra will

be totally different. This can be made clear by specifying a certain value for I and it will then be shown how a variation in I will affect the fine structure levels of the terms.

As an example of the type of fine structures which are to be expected in one-electron spectra, a case like that of sodium will be considered. Referring to Fig. 2 we see that the deepest lying term in sodium involves the most penetrating electron and is the $3s\ ^2S_{1/2}$ term. Next to it come the two terms $4p\ ^2P_{1/2}$ and $4p\ ^2P_{3/2}$ which only involve p electrons. We will examine the structures of the two lines $3s\ ^2S_{1/2} - 4p\ ^2P_{1/2}$ and $3s\ ^2S_{1/2} - 4p\ ^2P_{3/2}$. These two lines are the well known yellow D lines of sodium. For simplicity we shall assume that the nuclear spin I of sodium to be equal to $\frac{1}{2}$. This spin is to be coupled with each of the three terms concerned in producing the lines, in order to see what fine structure levels will arise. The $3s\ ^2S_{1/2}$ term has the J value of $\frac{1}{2}$ and as the spin I is $\frac{1}{2}$, it is obvious that I and J can only combine in two ways, to give $F = 0$ or $F = 1$ (it will be remembered that the maximum number of fine structure terms is $2J + 1$ or $2I + 1$ according to whether J or I is the smaller). The F value 0 is produced when the nuclear spin and the electron spin oppose each other, and the F value 1 arises when the two spins act parallel*. It follows therefore that the $3s\ ^2S_{1/2}$ term is double.

In this particular case $I = \frac{1}{2}$ and as all the J values in sodium are $> \frac{1}{2}$ every term of the spectrum must also be double. The $4p\ ^2P_{1/2}$ term will have the two F values 0 and 1 as in the previous case, but in the $4p\ ^2P_{3/2}$ term the F values will be 1 and 2, for J equals $\frac{3}{2}$ and I equals $\frac{1}{2}$, hence $F = 1$ or 2. Since both the lower and upper term of each of the two lines are double, each line will be a tiny multiplet. The fine structure of the common lower $3s\ ^2S_{1/2}$ term will be much wider than that of the upper terms, since an s electron is then involved. The structure of $4p\ ^2P_{1/2}$ will be somewhat greater than that of $4p\ ^2P_{3/2}$.

* The question as to true spin direction of an electron and of a spinning nucleus is somewhat modified by the wave mechanics, but for simplicity the vector model is adhered to here.

Remembering the selection principle, namely, $\Delta F = \pm 1$ or 0 ($0 \rightarrow 0$ excluded) it is seen from Fig 11 that each of the D lines will have three components. If the structures in the p terms are very small, and in sodium this is the case, the separations of the upper terms cannot be experimentally resolved and both lines appear to have the same structure, namely two components, the intensity ratio and frequency

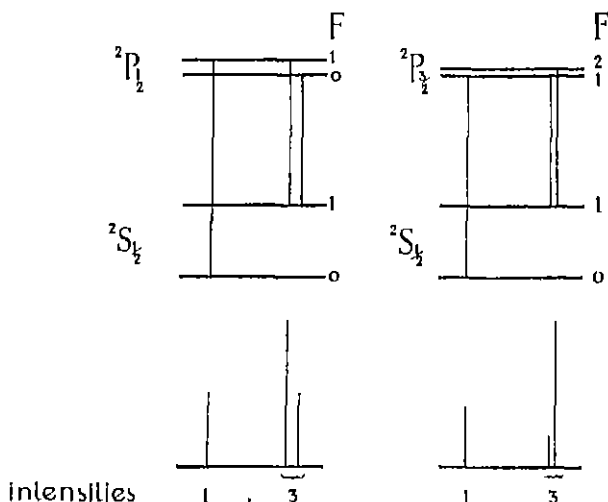


FIG 11 —Hypothetical fine structures of the sodium D lines, assuming that the nuclear spin is $\frac{1}{2}$. Because of instrumental difficulties in resolving power and natural line widths, both the D lines have the same apparent structure, namely doublets in which the intensity ratio is 3 : 1

separation being the same for both of the D lines. It has been shown by Fermi⁶ that in the s terms of one-electron spectra, the nuclear spin can be calculated from the intensity ratio of these apparent doublets, when the upper terms are unresolved. It can be shown that the quantum weight of a fine structure level is $2F + 1$. By this is meant that the sum of the intensities of all the lines

coming to a level of given F value is proportional to $2F + 1$. If I is the nuclear spin, the F values of the two fine structure levels of the $^2S_{1/2}$ term are $I + \frac{1}{2}$ and $I - \frac{1}{2}$ respectively. The intensity ratio of the two components of the doublet is therefore

$$\frac{2(I + \frac{1}{2}) + 1}{2(I - \frac{1}{2}) + 1} = \frac{I + 1}{I},$$

so that the accurate measurement of the intensity ratio will give the spin, I . Experimentally this is very difficult to determine, because the lines involved are resonance lines, which usually suffer self-absorption and this gives rise to false intensity measurements. In the case under consideration, the intensity ratio of the fine structure components in both the D lines would be 3 : 1. It is easy to see by making I equal to zero, that the formula given above is self-consistent. The intensity ratio in the fine structure doublet then becomes 1 : 0, meaning that one line is missing. In other words, the fine structure doublet becomes a single line when the atom has no nuclear spin, which is naturally what one expects. Measurements have been carried out upon intensity ratios of the fine structure doublets of alkali resonance lines,⁶ but the results are usually disturbed by reversal.

Effect of varying nuclear spins.

The calculated structure of the D lines becomes very different for different values of I , although the observed structure may not appreciably change. The latter effect is, however, only accidental and is due to the fact that the structure in the s electron term is so much wider than in that of the p electron. The pattern formed by a larger spin such as $\frac{3}{2}$ is shown in Fig. 12. The $3s\ ^2S_{1/2}$ term again divides into two levels, but as $J = \frac{1}{2}$ and $I = \frac{3}{2}$ the F values now become 2 and 3 respectively. The $4p\ ^2P_{1/2}$ term behaves in the same manner, except that the structure is on a smaller scale. As a result $3s\ ^2S_{1/2} - 4p\ ^2P_{1/2}$ has three components, two of which are grouped closely together.

With a nuclear spin of $\frac{1}{2}$ the $4p \ ^2P_{3/2}$ term is no longer double but becomes more complex. Since $J < I$, $2J + 1$ components are formed, so that with $J = \frac{1}{2}$ the term splits up into four components. We can see from Fig. 13 how these four levels can occur. The J value of the level is represented by the long thin arrow and the nuclear spin by the short thick arrow. In the highest level the two vectors are parallel, and in the lowest they are anti-parallel

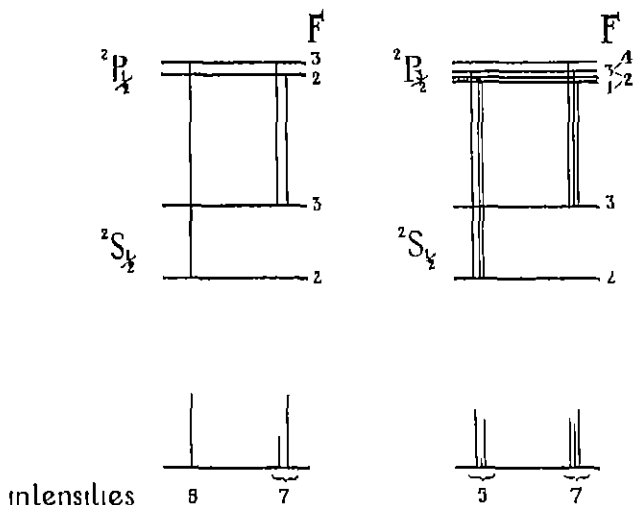


FIG. 12.—Hypothetical fine structure of sodium D lines with the assumed nuclear spin of $\frac{1}{2}$. Two doublets are formed, the separation being 0.06 cm^{-1} , and the intensity ratio 5:7.

In between these values, the vectors take up intermediate positions that satisfy the cosine law. Expressed simply, this means that the angles between the vectors are such that the resultant vector F can have all *integral* values between 4 and 1. As shown in the diagram we obtain four levels with F values 1, 2, 3, 4, the smallest F value lying deepest. These levels will be so spaced as to obey the Landé interval rule, although this is not shown in the

schematic vector diagram, but it is so drawn in Fig. 13. It is seen in this figure that the line $3s\ ^2S_{1/2}-4p$ has six components in its fine structure pattern. The components are grouped into two pairs of threes, owing to the smallness of the upper interval factor. If the interval

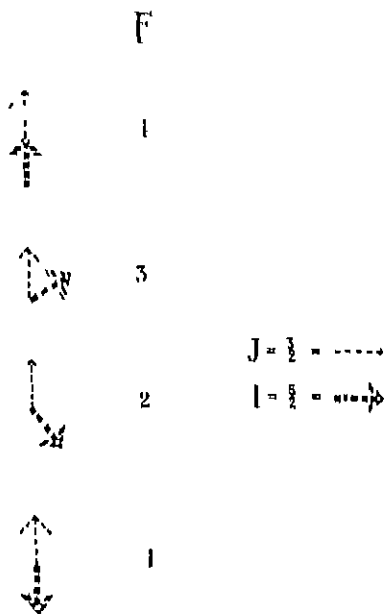


FIG. 13 — Illustrating the vector coupling between a nuclear spin $I = \frac{1}{2}$ with a $J = \frac{3}{2}$ to form four fine structure levels.

be made, and when $I > J$ of checking the results by examination of other terms.

When the nuclear spin of an atom is small, the structures are simple, and the line patterns not very complicated, but when the spin is large, the terms with high J values become quite complex and the line patterns

factors of the terms are both small compared that of the lower the patterns can completely resolve and the structure both the D line doublets with intensity ratio 5, of approximately same separation was obtained was taken to The above values, are taken for transition only nuclear spin sodium is now known to be $\frac{3}{2}$. This experiment shows that the importance of experimentally resolving the components

line before a reasonable estimate of the nuclear spin of the atom

spondingly more so. Fortunately the interval factor in one of the terms of a line is often very much smaller than that in the other term and this introduces a considerable simplification into the line pattern which is formed.

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CHAPTER V

FINE STRUCTURE IN MANY-ELECTRON SPECTRA

Two-electron spectra

The calcium atom will be chosen to illustrate the structures expected in a two-electron system. No structure has so far been found in the odd isotope of calcium, but this is due to various causes which need not be considered here. As in the case of sodium the type of structure in the terms will depend upon the numerical value of the nuclear spin, but there are one or two features of special interest which are not dependent on this and these will be discussed first.

Reference to Fig. 6 shows that there are a number of sets of terms in calcium which go to different series limits and it is necessary to consider these separately. The most important terms are those which go to the $4s\ ^2S_{1/2}$ limit. It will be remembered that the group of terms which go to this limit is produced when one of the valence electrons remains in a $4s$ orbit and the other moves to higher orbits. Since the electron configuration for each level of this group possesses a penetrating $4s$ electron, it will be expected that all the terms will show wide fine structure splittings, where term splitting is possible. This is generally true, although in some terms the moment of the optical electron opposes that of the $4s$ electron and thereby reduces the coupling with the nucleus.

The terms going to the $4s\ ^2S_{1/2}$ limit are $^1(SPD\ \dots)$ and $^3(SPD\ \dots)$ and of these the 1S_0 and the 3P_0 terms illustrate an important point. Since in these terms $J = 0$, then $2J + 1 = 1$, meaning that the fine structure multiplicity is one, or that the terms are single. This

result is obvious, because the spin I can only add to a zero J value to form a single F value equal to I . *No matter what the nuclear spin may be, all spectral terms with J value equal to zero show no fine structure* For all the other terms

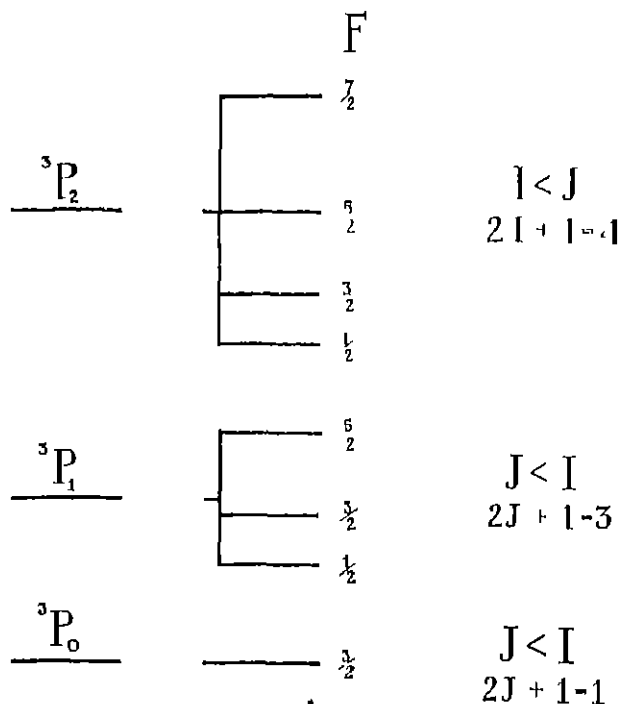


FIG. 14.—The fine structures of 3P terms when the nuclear spin is $\frac{1}{2}$. The number is $2I + 1$ or $2J + 1$, according to which is the smaller.

I and J compound in the usual manner to form multiplets. Suppose, for example, the nuclear spin is $\frac{1}{2}$, then the 3P_0 term will be single, the 3P_1 term will have three components, and the 3P_2 term will have four, as shown in Fig. 14.

Since all the terms which go to the $4s\ ^2S_{1/2}$ limit have a $4s$ electron in their configurations, the structures of all will be wide (excluding terms with $J = 0$). It is seen from this that a line transition such as $4s\ 4p\ ^3P_2 - 4s\ 4d\ ^3D_2$ will have structures of the same order in both the upper and lower terms. The result is that the line pattern is complex, as, for example, in the case shown in Fig. 10. Most of the terms which go to the next limit, $3d\ ^2D_{3/2}$, of the calcium atom, do not possess a penetrating $4s$ electron in their configurations, so that practically all the terms going to this limit have narrow structures, and the same is true of the terms which go to the next limit. Line transitions between one of the terms which go to the $4s\ ^2S_{1/2}$ limit and one of the terms which go to another limit have their patterns much simplified, as was the case with the sodium lines in Fig. 12. *The lines which arise from transitions between two terms, neither of which possess unpaired s electrons in their configurations, often appear single, because the fine structure is so minute.* Generally speaking, the appearance of the structures is very dependent on the specific electrons in the configurations.

General vector method for many-electron spectra

A very convenient method for predicting the fine structures which arise in atoms with complex electron configurations has been developed by White¹. This is an extension of the vector method which has already been used to show how gross structure multiplets arise. It was shown in Chapter III that the best way to see how the gross structure multiplets arise was by adding the vector representing the optical electron to the ion terms. The fine structures are obtained by the simple extension of adding the nuclear spin vector to the terms already obtained in this manner. In a large number of cases only the configurations which possess a penetrating s electron show any structure in the terms, so that this type of term will be considered first.

If a configuration possesses a penetrating s electron, it can be shown that the coupling between the nuclear spin

and the electron configuration is proportional to $\cos(\mathbf{Is})^*$ and not, as in general, to $\cos(\mathbf{IJ})^2$. The direction of the coupling between the nuclear spin and the s electron becomes of great importance, so that it is necessary to know exactly in which direction the s electron is pointing with reference to the other electrons of the configuration. For this reason the series limits must be known and the multiplet structure built up from the ion, in order that the coupling of the s electron can be followed carefully from term to term.

For the purpose of explaining the vector method, recourse will be made to Fig. 9, which shows how the 2P and 4P multiplets of the $4s^2 4p^4 5s$ configuration of Br I are formed. The problem is to see how the addition of the nuclear spin affects the terms. The terms are split up according to the J values, but the interval factors, on which the coarseness of the structures depend, are determined by the value of $\cos(\mathbf{Is})$. White assumes that the complex electron group $4s^2 4p^4 5s$ behaves as a unit and couples with I in the usual vector manner, the degree of coupling depending on the orientation of I and s . The relative values of the interval factors, in a group of levels belonging to a gross structure term, are proportional to $\cos(\mathbf{Is})$ when $\cos(\mathbf{IJ}) = 1$. That is to say, when the nuclear spin is set parallel to J the angle which I then makes with the spin s of the $5s$ electron determines the coarseness of the structure. From the properties of vectors we have

$$\cos(\mathbf{Is}) = \cos(\mathbf{IJ}) \times \cos(\mathbf{Js}),$$

and as $\cos(\mathbf{IJ}) = 1$ when I and J are parallel, therefore $\cos(\mathbf{Is}) = \cos(\mathbf{Js})$.

As the coarseness of the structures is proportional to $\cos(\mathbf{Is})$ it must therefore also be proportional to $\cos(\mathbf{Js})$, hence the problem is to find the relative orientation of the spin of the s electron, with respect to the resultant J value

* s is the spin vector of the s electron. It is assumed throughout that LS coupling is used.

of the term, and the angle between these vectors determines the coarseness of the structures

As in the two electron spectra the *number* of fine structure levels in any gross structure term is determined by the values of I and J . There will be $2I + 1$ or $2J + 1$ levels according to which is the smaller value. From the Landé formula it is easy to see by subtraction of two levels, that the actual separation between two levels of fine structure quantum numbers $F + 1$ and F is $A(F + 1)$, A being the interval factor for the term in question. When I and s are parallel $\cos(I s) = 1$ so that A is positive. When I and s are anti-parallel $\cos(I s) = -1$ so that A is negative. *A negative value for A means that the fine structures are inverted, the highest F value lying deepest.* The vector method will now be applied to bromine in order to trace through the various possible couplings.

Fig 15 shows the vector combinations. The notation is exactly the same as in Fig. 9* and in reality A and B of Fig 15 are identical with those of Fig 9. A shows the 3P terms of Br II based upon the $4s^2 4p^4$ configuration and B shows the $5s$ 3P and $5s$ 4P terms for Br I which are formed by the addition of the $5s$ electron. The vector process up to this point has already been discussed in detail. The experimental value for the nuclear spin of bromine is $\frac{3}{2}$ and C shows the fine structure levels (dotted) that should arise when a spin of $\frac{3}{2}$ is added to the doublet and quartet multiplets. In order to simplify the complicated vector diagrams, only the coupling between the nuclear spin and the $5s$ electron is shown at the extreme right. As before, the thin dotted arrow in B shows the direction of J . I is set parallel to this, so as to conform to the rule that $\cos(I J) = 1$ and in this position the interval factor is proportional to the cosine of the angle between I and s . The spin of the s electron is shown, as before, by the hollow arrow, and the nuclear spin by the long thick dotted arrow.

* In configurations of the type $4s^2 \cdot 4p^4$ $5s$ and $4s^2 \cdot 4p^4$ $5p$, etc., it is often customary to omit the $4s^2 \cdot 4p^4$ for the sake of brevity, and only the optical electron $5s$ or $5p$, etc., is retained in the term notation.

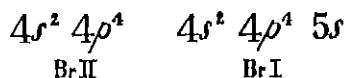
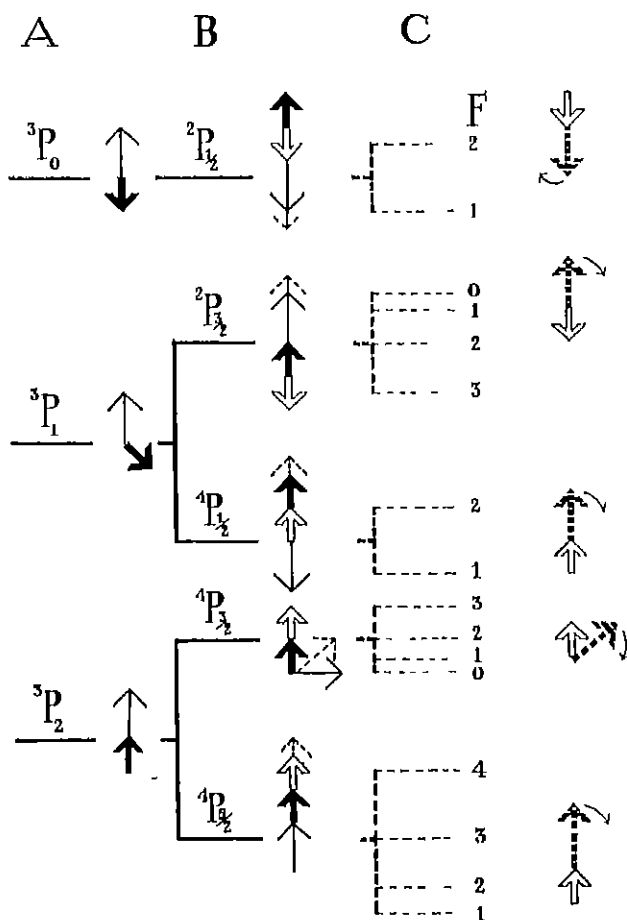


FIG. 15 — Vector coupling diagram showing how the fine structures in the $4s^2 4p^4 5s$ configuration are produced by a nuclear spin of $\frac{1}{2}$.

The small curved arrow at the head of this implies that it is to be compounded vectorially

Considering each term in detail it is seen that the $5s\ ^3P_{1/2}$ term has \mathbf{I} parallel to \mathbf{s} , and as $\mathbf{J} = \frac{1}{2}$ the fine structure is therefore a wide normal doublet, wide because the two spin vectors assist, and normal since they act parallel. In the next term $5s\ ^3P_{3/2}$, the \mathbf{I} and \mathbf{s} oppose, so that the term is inverted. As $\mathbf{J} = \frac{3}{2}$ a quartet term is formed, and the structures are still comparatively large. The $5s\ ^4P_{1/2}$ term is again a wide normal doublet. The next term is $5s\ ^4P_{3/2}$ and the nuclear spin acts at an angle with the s electron spin so that a medium width quartet is produced. Finally the $5s\ ^4P_{5/2}$ term has all the vectors parallel, so that a wide quartet is formed.*

The methods used to describe the coupling in the case of a penetrating s electron can be applied to the case of a non-penetrating p electron. For instance, it is possible to couple the $5p$ electron to the $4s^2\ 4p^4$ core of Br II, but it is found that the agreement with experiment is not very good. The supporting evidence for the s electron case has been very well established in manganese, but different investigations indicate that such a simple treatment is not possible for p electrons. It is quite certain that the p electrons couple vectorially to give the correct number of levels that theory demands.

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* There is reasonably good experimental verification for bromine, the deviations being due to the incomplete LS coupling. In manganese, which shows full LS coupling, the vector method is completely verified. Bromine has only been selected as an example of a many-electron atom, for illustration purposes.

CHAPTER VI

ANALYSIS OF THE FINE STRUCTURES

Intensities of fine structure components

Although it is true that perturbations may occur in fine structure levels most of the spectra hitherto investigated seem to show the interval rule to be valid. The perturbations have been found in the fine structure of mercury, bismuth and aluminium and will be discussed later, but for the present purpose all that need be said is that in certain cases the fine structure in a term can be perturbed by a neighbouring term in such a manner that the interval rule fails. The intensities of the fine structure components of a line are just as important as the intervals, and are of equal help in the analysis. Perturbations have been found in intensities, but so far these have not been very serious. The intensity disturbances are of two kinds. In one case they are due to the source being possibly too hot, or the pressure too high, with resulting self reversal effects. The other type of intensity perturbation is not understood, but will be discussed in the chapter dealing with perturbation.

The intensity rules which fine structure components obey are important. These have been given by Hill¹ and since they are used so frequently in analysis, it has been considered worth while to reproduce them here. They form the basis of the graphical method of analysing fine structures, due to Fisher and Goudsmit,² which is extremely useful in practical work. In the formulæ given below the following abbreviations are used. $I_n(F \rightarrow F-1)$ means the intensity of a line transition from an upper term fine structure F level to a lower term fine structure level $F-1$.

The meanings of $\text{In.}(F \ F)$ and $\text{In.}(F \ F - 1)$ are then self-evident. In all cases the first F value refers to the upper term, and the second to the lower term. In the formulæ themselves the following contractions are used for the sake of brevity —

$$\begin{aligned} P(a \ b \ c) & \quad (a + b)(a + b + 1) - c(c + 1), \\ Q(a \ b \ c) & \quad c(c + 1) - (a - b)(a - b + 1), \\ R(a \ b \ c) & \quad a(a + 1) + b(b + 1) - c(c + 1) \end{aligned}$$

All the transitions are those for which $\Delta L = \pm 1$, and there are three sets of formulæ according to whether ΔJ is equal to $+1$, 0 , or -1 . These are set out in table form below. A , B , and C are constants determining the relative intensities of the gross structure lines but do not here concern us, since all the components for any one given line (i.e. single J transition) involve the same constant so that the intensity ratios in a fine structure pattern are not dependent on the value of the constant.

On substituting in these formulæ one finds that *the transition $\Delta F = 0 \rightarrow 0$ always has zero intensity, and also that the total intensity of all the components to a given F level is proportional to $2F + 1$* . The formulæ appear rather cumbersome, but are actually simple to apply, and check themselves automatically, so that errors in calculation are avoided.

Irregular and regular line patterns.

As a result of the intensity and interval rules, two types of line patterns are produced, and these may conveniently be called irregular and regular patterns. An irregular line pattern arises when both the upper and lower interval factors are of the same order. The line pattern becomes particularly complex when the fine structure multiplicities are high. The irregular structures can only be analysed by seeking for frequency differences, as in the case of gross structure multiplets. When the fine structure multiplet has been built up the F values of the terms are easy to find if $J > I$, but if $J < I$ the F values can usually only be

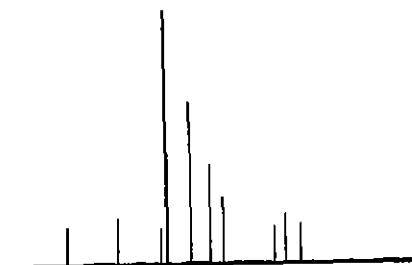
obtained from the interval rule. If both I and J are already known, the analysis of a line is much simpler. However, when the F values have been found I can at once be calculated. The best way to analyse a spectrum with many lines is to select the lines which involve terms wherein the J value is greater than the suspected I value. In all of these terms the multiplicity is $2I + 1$, so that I is determined when the line pattern has been analysed, and the interval rule can be applied as a check. It is often quite impossible to analyse the pattern of a line completely in this manner, because many fine structure components crowd together and cannot be resolved. The method has, however, been successfully used in very many cases, e.g. Cd, Tl, Pb, Hg³ etc. An example of an *irregular* fine structure pattern is shown in Fig. 16(a). The line pattern illustrated is that of $5s^2\ ^4P_{1/2} - 5p\ ^4D_{3/2}$ in Br I. The nuclear spin is $\frac{3}{2}$ and for the purpose of illustration it is assumed that the interval factor of the upper term is $\frac{1}{2}$ that of the lower. The resulting pattern is complex, and no obvious apparent regularities exist in it.

In the irregular pattern described above, the irregularity

Transition	$\Delta L = \pm 1$ $\Delta J = +1$	$\Delta L = \pm 1$ $\Delta J = 0$	$\Delta L = \pm 1$ $\Delta J = -1$
$\text{In.}(F, F+1)$	$A \frac{P(F+1, J, I) P(F+2, J, I)}{F+1}$	$B \frac{P(F+1, J, L) Q(F, J, I)}{F+1}$	$C \frac{Q(F+1, J, I) Q(F, J, L)}{F+1}$
$\text{In.}(F, F)$	$A \frac{2F-1}{F(F+1)} P(F-1, J, L) Q(F-1, J, L)$	$B \frac{2F+1}{F(F+1)} [R(F, J, L)]^2$	$C \frac{2F+1}{F(F+1)} P(F, J, L) Q(F, J, L)$
$\text{In.}(F, F-1)$	$A \frac{Q(F-1, J, I) Q(F-2, J, L)}{F}$	$B \frac{P(F, J, L) Q(F-1, J, I)}{F}$	$C \frac{P(F, J, I) P(F-1, J, I)}{F}$

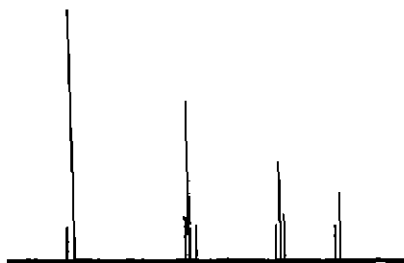
arises from the fact that the two interval factors have nearly equal values

Irregular



Interval factor ratio 5 4

Regular



Interval factor ratio 20:1

FIG 16—Dependence of the appearance of a fine structure line pattern on the fine structure interval ratio of the upper and lower terms

It is at once apparent that a regular

It often happens that only one term involves a penetrating s electron, and so produces a structure which is very much coarser than the structure in the other term. When this is the case the line pattern becomes *regular* and has the appearance of a regular degraded series. For example, the same line as above has the pattern shown in Fig 16(b) when the interval factor of the upper term is only $\frac{1}{20}$ th that of the lower. Owing to the natural widths of the components, and partly because of imperfections in the instruments used, the closely packed components cannot usually be separated, so that a regular quartet pattern will be seen in the present example. It is at once apparent that a regular pattern will usually

show the structure of one of the terms only (exceptions occur) In the present instance the structure is that of the lower term, which involves the s electron * This *term* is therefore quartet in structure, and as the J value is $\frac{3}{2}$, then I must be equal to $\frac{3}{2}$, because a greater nuclear spin would have produced more components. This line shows how a nuclear spin can often be very easily obtained from one regular pattern The scale of the structures may be gathered from the fact that the total width of the structure is about 0.4 cm^{-1}

Graphical method of analysis

In the regular "pseudo quartet" just described there are actually *ten* components, and the appearance of the line pattern becomes more and more complicated as the relative value of the smaller interval factor increases, with respect to the larger In order to deal with complex patterns which are incompletely resolved, a very valuable graphical method of analysis has been proposed by Fisher and Goudsmit ² For this graphical method I and the J of both terms must be known for the line in question It is often possible to get I from the other data, e.g. from the structure of favourable lines or from band spectra, etc., so that the method is generally applicable The same line, namely

$$5s \text{ } ^4P_{3/2} - 5p \text{ } ^4D_{3/2}$$

of Br I, will be taken for an example of the use of this graphical method

The graph is shown in Fig. 17 Firstly the interval factors of both the upper and lower terms are made equal, and the complete multiplet drawn The position of each component of the *line* pattern is plotted as a point along the line AB Secondly, the upper term is completely inverted, the interval factor being kept unchanged, and the new resulting multiplet drawn The position of each component of the new *line* pattern is plotted as a point along the line EF. Corresponding points, that is, points which

* This example is taken from the actual experimental data in Br I,

represent the same F transitions, are joined up by straight lines. For preliminary visual analysis the widths of these lines are made roughly proportional to the intensities of the transitions as calculated from Hill's formulæ. For the purpose of calculation, thin lines can be used, the actual intensity ratios being written in. The points which represent the upper limit of the whole graph, along AB, show the line pattern given by the two terms in question, when the interval factors of the two terms are identical, in other words, when the interval factor ratio is $+1$. Similarly, the points at the lower limit of the graph show

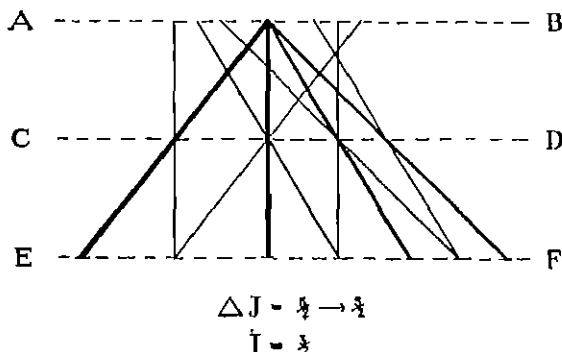


FIG 17 — Fisher-Goudsmit line complex for the transition $J = \frac{3}{2} \rightarrow \frac{1}{2}$. The nuclear spin is $\frac{3}{2}$ in this example

the line pattern when the ratio of upper to lower interval factors is -1 . The horizontal line CD cuts the graph at the centre. Each line is cut at a point, and each point represents a component of the *line* pattern. This particular centre pattern is that formed when the upper interval factor is equal to zero [since CD lies midway between the lines AB and EF which represent ratios of $+1$ and -1 respectively]. For any given ratio of interval factors, the *line* pattern is determined by drawing a horizontal line through the graph at a point between AE corresponding to this ratio. Thus, for example, the line patterns of Fig 16

were obtained by drawing horizontals at points corresponding to interval ratios of $\frac{1}{8}$ th and $\frac{1}{16}$ th respectively, the upper interval being the smaller in both cases. When a line pattern has been measured all that need be done is to fit it unambiguously into the graph, and the values of both the upper and lower interval factors are at once determined, although the resolution in the line pattern may be incomplete.

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CHAPTER VII

TERM INTERVAL FACTORS

Coupling of two s electrons

From the calculated interval factors important information can be obtained concerning the coupling processes of the individual electrons, and perturbation effects can be detected. Extensive theoretical calculations of the ratios of the interval factors of the different terms of a spectrum have been made by Goudsmit. From the experimental side, although data are lacking, enough has been found to show that the agreement between theory and observation is only partial. Discrepancies arise from the fact that the actual coupling process between a nucleus and an electron is unsufficiently understood. Fermi, Casimir, Breit, and Goudsmit¹ have all made different attempts to solve this mathematical problem, which presents grave difficulties.

There is general agreement for the case of the atom which possesses one valence electron, such as the alkali metals or ionised alkali earths. Theory shows that the interaction energy between the nucleus and the optical electron is of the form $E = A \mathbf{IJ} \cdot \cos(\mathbf{IJ})$. This leads to the Landé interval rule for the fine structures, and experimental observations support this strongly. Casimir showed that in the particular case of an s electron, the interaction energy is given by $E = A \mathbf{Is} \cos(\mathbf{Is})$ and this fact has already been utilised. Following Casimir, Goudsmit has calculated the interaction energy for an atom which has two valence s electrons². For example, all the 3S_1 terms of Ca I, are terms of an atom which has two s electrons in

its configuration. The interaction between the nucleus and the spins of the two electrons, s_1 and s_2 , is

$$E = a_1 I s_1 \cos(I s_1) + a_2 I s_2 \cos(I s_2)$$

The energy is treated as the sum of two interaction energies, one for each electron. Each electron obeys the law deduced by Casimir, and in the equation, a_1 and a_2 are the numerical proportionality factors for each electron*. The cosines are to be averaged over a complete electron revolution and when this is done the formula reduces to

$$E = I J \cos(I J) \left[\frac{a_1 s_1}{J} \cos(s_1 J) + \frac{a_2 s_2}{J} \cos(s_2 J) \right],$$

J , having the usual significance, being here the resultant of s_1 and s_2 . Comparing this with the previous general equation, namely,

$$E = \Lambda I J \cos(I J),$$

it is at once evident that the two s electrons obey the same general law as one electron, if the interval factor Λ is replaced by the expression in square brackets. When the quantum values of the cosines are substituted in the expression for Λ we get

$$\Lambda = a_1 \frac{J(J+1) + s_1(s_1+1) - s_2(s_2+1)}{2J(J+1)} + a_2 \frac{J(J+1) + s_2(s_2+1) - s_1(s_1+1)}{2J(J+1)},$$

since $s_1 = s_2 = \frac{1}{2}$, this reduces to

$$\Lambda = \frac{1}{2} a_1 + \frac{1}{2} a_2$$

Thus, the term interval factor Λ is half the sum of the proportionality factors of the two electrons. Experimental verification of this has been possible in a few cases. Thallium I. has been examined and the interval factors for the fine structures of the terms of the $6s$, $7s$, $6p$, $8s$, and $6s$, $9s$, etc., configurations determined. From these it is possible to calculate the value of a_1 for the $6s$ electron and of a_2 ,

* That is to say, the "interval factor" for the individual electron.

a_3, a_4 , etc., for the $7s, 8s, 9s$, etc., electrons. The value of a_1 increases slightly as the second electron approaches the ionising limit because the screening effect of the second electron diminishes. a_1 tends to a limiting value which can be calculated. In the Tl II atom, which possesses one electron in the $6s$ orbit, the value of a_1 should be identical with the limiting value of a_1 calculated from the Tl I spectrum. Allowance has to be made for the fact that the interval factor is proportional to z^2 , where z is the degree of ionisation. More strictly the interval factor is (see page 38) proportional to $Z_1 z^2$, but in a heavy atom Z_1 is sensibly the same for the normal and the ionised atoms so that the coarseness of the structure is very nearly proportional to z^2 *. The values of a_1 calculated from Tl I and Tl II, agree within experimental error, so that the theory is supported³.

Interval factors for the general case

The general theory for the fine structure interval factors in spectra, which show LS or jj coupling, has been worked out by Goudsmit,⁴ and since it is not practicable to give any details of his calculations here, only a few of his results will be quoted. The calculations lead to entirely different results in LS coupling and in jj coupling, the results being more satisfactory for the latter type. In LS coupling it is only possible to give the sum of the interval factors for all the terms of a multiplet group which have the same J value. For example, the 1P and 3P terms which arise from an s, p electron configuration are $^1P_1, ^3P_0, ^3P_1, ^3P_2$. The interval factor for 3P_0 is zero, that of 3P_2 can be calculated, but only the sum of the interval factors for the two terms 1P_1 and 3P_1 is obtained from the formulae, for they have identical J values.

The following table gives some of the more important results. a is the proportionality constant for the p electrons and b the constant for the s electrons in any configuration.

* This is obviously an important practical point, for the higher the degree of ionisation, the coarser are the structures and therefore the easier to observe.

The value of a or b is the same for all *equivalent* electrons. In the table only a selected group of results has been shown and for full details the original paper must be consulted.

The calculated values for the interval factors of spectra which show *jj* type of coupling are more satisfactory than those for *LS* type, because the interval factor for every

TABLE III

Interval factors in LS coupling

Interval factor for p electron		a
Interval factor for s electron		b
Configuration	J	Interval Factor = Λ
p and p^3	$\frac{3}{2}, \frac{1}{2}$	$\Lambda = \frac{1}{2}a$ $\Lambda = \frac{3}{2}a$
p^2 and p^4	2 1	$\Sigma\Lambda = 1\frac{1}{2}a$ $\Lambda = 0a$
p^3	$\frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\Lambda = \frac{3}{2}a$ $\Sigma\Lambda = 1\frac{1}{2}a$ $\Sigma\Lambda = 2\frac{1}{2}a$
$p\ s$ and $p^3\ s$	2 1	$\Lambda = \frac{1}{2}a + \frac{1}{2}b$ $\Sigma\Lambda = 2a + \frac{1}{2}b$
$p^2\ s$ and $p^4\ s$	$\frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\Sigma\Lambda = 1\frac{1}{2}a + \frac{3}{2}b$ $\Sigma\Lambda = 1\frac{1}{2}a - \frac{1}{2}b$ $\Sigma\Lambda = 0a - 1\frac{1}{2}b$
$p^3\ s$	3 2 1	$\Lambda = \frac{1}{2}a + \frac{1}{2}b$ $\Sigma\Lambda = 2a + \frac{1}{2}b$ $\Sigma\Lambda = 2\frac{1}{2}a - \frac{1}{2}b$

term is given separately. The s electron has the same proportionality constant b as in the *LS* coupling, but the p electrons are different. As *jj* coupling implies that each electron has a separate j value, there are two types of p electron, namely $p_{1/2}$ and $p_{3/2}$. These two electrons differ because in the one the l and s oppose, so that j is equal to

$\frac{1}{2}$, and in the other l and s are parallel in direction, so that j equals $\frac{3}{2}$. These two types of electron are different in so far as the $p_{1/2}$ electron is more penetrating than the $p_{3/2}$ electron, so that different proportionality constants enter the formulæ for each. The constants will be called a'' for the $p_{1/2}$ electron and a' for the $p_{3/2}$ electron. According to theory these constants are not independent, but are related to the constant a of the p electron in LS coupling

TABLE IV

Interval factors in jj coupling

Interval factor for $p_{1/2}$ electron	a''
Interval factor for $p_{3/2}$ electron	a'
Interval factor for s electron	b

Configuration	j	J	Interval factor
p^3 and p^3	$\frac{1}{2} \quad \frac{1}{2}$	2	a'
	$\frac{3}{2} \quad \frac{1}{2}$	2	$\frac{1}{2}a' + \frac{1}{2}a''$
	$\frac{3}{2} \quad \frac{3}{2}$	1	$\frac{1}{2}a' - \frac{1}{2}a''$
$p^2 s$ and $p^2 s$	$\frac{1}{2} \quad \frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}a' + \frac{1}{2}b$
	$\frac{3}{2} \quad \frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}a' - \frac{1}{2}b$
	$\frac{3}{2} \quad \frac{3}{2}$	$\frac{5}{2}$	b
	$\frac{1}{2} \quad \frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}a' + \frac{1}{2}a'' + \frac{1}{2}b$
	$\frac{3}{2} \quad \frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}a' - \frac{1}{2}a'' - \frac{1}{2}b$
	$\frac{1}{2} \quad \frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}a' - \frac{1}{2}a'' + \frac{1}{2}b$
	$\frac{3}{2} \quad \frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}a' - \frac{1}{2}a'' - \frac{1}{2}b$

Theory gives

$$a' = \frac{8}{5}a,$$

$$a'' = \frac{2}{3}a,$$

therefore

$$a' = \frac{1}{3}a''.$$

As an example of the interval factors calculated for jj coupling, see Table IV. The first column in this table gives the electron configurations, and the second column the j values of the individual electrons. The j value of the s electron is omitted, since it is always equal to $\frac{1}{2}$. In

the third column the final resulting possible J values are shown, and opposite each J value (in the fourth column) is the calculated interval factor of the term. The terms with $J = 0$ are omitted as the interval factor for such a term is zero.

Interval factors in multiply ionised spectra

So far there is not a great deal of experimental evidence which has a bearing on the verification of the Goudsmit formulæ, since only few spectra have been thoroughly examined. Of great interest are the results which have been obtained in the spectra of bismuth.⁴ In bismuth the B_1 I, B_1 II, B_1 III and B_1 V spectra have all been studied. It has been possible to calculate the proportionality constants of the separate electrons when different neighbouring electrons are present. Thus, in B_1 I the $6p^3$ and the $6p^2 7s$ configurations give the values of a'' , a' and b' for the $6p_{1/2}$, $6p_{3/2}$ and $7s$ electrons respectively.* In B_1 II the configurations examined were $6s 7s$, $6p 6d$ and $6p 7p$, so that the constants for the same electrons could be calculated, as well as those of $7p_{1/2}$ and $6d$. The B_1 III spectrum gave data for the $6s 6p^2$ configuration, so that in addition the constant b for $6s$ was determined. Finally, the $6s$ configuration of B_1 V also gave a value for the constant b . A convenient summary of the results is shown in Tables V and VI.—

TABLE V
 s electrons

		Spectrum			
Electron	Constant	B ₁ I	B ₁ II	B ₁ III	B ₁ V
$6s$	b	1.6	1.6	1.8	2.6
$7s$	b'	0.116	0.352	0.472	—

* Bismuth shows jj coupling in these terms

For both the $6s$ and $7s$ electrons the value of the constant increases regularly with the increase in the degree of ionisation. This is due to the removal of screening outer electrons. Table VI gives a summary of the observations made on the p electrons, —

TABLE VI

 p electrons

Electron	Constant.	Spectrum.		
		BI I	BI II	BI III
$6p_{1/2}$	a''	0.375 0.390	0.430 0.565 0.462	0.66
$6p_{3/2}$	a'	0.008 0.026	0.028	0.01
$7p_{1/2}$	a'''		0.012	

It was possible to calculate a' and a'' from more than one term, and as seen in Table VI there is good approximate agreement between these. The general conclusions to be made from the tables are as follows —

- (1) The constant for a given electron is bigger the higher the degree of ionisation, owing to the removal of screening effect as other electrons are removed from the configurations.
- (2) The constant for an electron falls rapidly in value when the total quantum number, n , of the electron increases.
- (3) The constant for the $p_{1/2}$ electron is very much greater than that of the corresponding $p_{3/2}$ * electron, the ratios of these constants being altogether much greater than the calculated value, 5.1.

* The exact value of the $p_{3/2}$ electron constant was difficult to determine, but the data showed unambiguously that it was relatively quite small.

The fact that a'' is very much greater than $5a'$, which the simple theory at first predicts, is extremely interesting. There are two possible explanations, the second of which is much more likely than the first. It is possible that, owing to insufficient knowledge of the interaction processes, the equations are wrong, and the calculated values of a' and a'' are not genuine. However, against this is the fact that the methods used to deduce the formulæ have given correct results when applied to gross structure multiplet data, and also to other fine structure data. This explanation is therefore not very probable. A much more likely explanation has been suggested by Breit,⁵ who has shown by means of a wave mechanics treatment, that in heavy atoms a $p_{1/2}$ electron behaves with respect to the nucleus as if it were a deeply penetrating electron. The effect is only marked in the heavier atoms, as it arises from second order corrections which are negligible when the atomic weight is small. If the $p_{1/2}$ electron behaves as if it were penetrating, it will therefore have associated with it a very large interval factor, comparable, in fact, with that of the s electron. As seen from the data in bismuth this is the case, so that Breit's theory offers a reasonable explanation of the relatively great value of a'' . (The examination of the fine structures in the As II spectrum⁶ tends to confirm this.) It is, of course, of great practical importance, as the penetrating property of the $p_{1/2}$ electron results in the production of structures far wider than at first expected on the simpler theory.

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CHAPTER VIII

ISOTOPE EFFECT

Isotope effect in bands

Up to the present any fine structure effect arising from the existence of isotopes has been neglected in the discussion. The isotope effects have become very important from both the experimental and theoretical aspects, so they will be treated here in some detail. The first attempt to detect any isotope effect in line spectra was made by Aronberg,¹ who found that the wave-length of the lead line λ_{4508} was slightly less in ordinary lead than in radium lead. He was not able to observe the true structure of the line, partly because the line was broadened in the source he used, and partly because the resolving power he employed was not very high. It was only later and more refined work that enabled the true isotopic effect in lead to be discovered.

The isotope effects in *line* spectra are always small, but the isotope displacements which occur in some *band* spectra are very large indeed, and are very easy to recognise. This arises from the fact that the positions of the vibration heads of an electronic band system depend upon the moment of inertia of the nuclei of the molecule, and are very sensitive to changes in the value of this moment of inertia. For example, boron has the two isotopes B_{10} and B_{11} so that the band spectrum of the oxide consists of two sets of bands, one due to $B_{10}O_{10}$ and the other to $B_{11}O_{10}$. The different boron atoms have different moments of inertia because of their different weights. The band constants differ markedly, therefore, so that the band heads of the one system are displaced from those of the other by

large amounts. Displacement of the order of 20 cm^{-1} are not unusual in band spectra, and it will therefore be seen that experimental observation of isotope effect in band spectra is much easier than in line spectra. Altogether the spectroscopic study of isotopes has, of course, to be carefully co-ordinated with Aston's mass spectrograph data.

Mass effect in line spectra

The first effect that was successfully found and interpreted was the *simple mass effect*. This effect was predicted by Bohr's theory, which showed that the positions of the lines of a spectrum depend upon the mass of the nucleus of the atom. A change in the mass of the nucleus causes a slight shift of the position of a line, so that if an atom consists of two isotopes, with different masses, all the lines of the spectrum will be duplicated. Calculation shows that the expected duplication will usually be very small, and must be sought for as a fine structure. As an example of the approximate method of calculation, the mass isotope effect to be expected in neon will be calculated.

In general the series terms of a spectrum can be fitted into a Hick's formula which is of the form

$$E = \frac{Rz}{\left(n + a + \frac{b}{n^3}\right)^2}.$$

In this formula a and b are simple numerical constants, n is the effective quantum number, z is the effective nuclear charge, and R is Rydberg's constant. The value of the Rydberg number is not quite constant, but involves the reduced mass of the electron, which is $\frac{mM}{m+M}$, where m and M are the mass of the optical electron, and the whole nucleus respectively. Neon mainly consists of two isotopes of masses 20 and 22*. The electron systems in these atoms are identical, so that the series will also be identical,

* Isotope 21 is too weak to be taken into consideration here

but as the Rydberg numbers differ slightly, one of the series will be relatively displaced, so that all the lines will show a fine structure. The calculation of the displacement is as follows

The frequency of a line is the difference of energy between two terms divided by Planck's constant, so that $\nu = R(A)$, where ν is the frequency, R the Rydberg constant, and A is of the form

$$A = \frac{z}{h} \left[\frac{1}{\left(n_1 + a + \frac{b}{n_1^2}\right)^2} - \frac{1}{\left(n_2 + a + \frac{b}{n_2^2}\right)^2} \right]$$

For the isotopic constituents of a line A is constant, since it does not involve the nuclear mass. The only variable factor is R . It follows then, that

$$\nu_{20} = R_{20}(A),$$

$$\nu_{22} = R_{22}(A),$$

hence

$$\nu_{22} - \nu_{20} = (R_{22} - R_{20})A$$

But $\nu_{22} - \nu_{20}$ is the difference between the two isotopic components of the line, i.e. the isotopic separation $\Delta\nu$, hence

$$\Delta\nu = R_{22}(A) \left[1 - \frac{R_{20}}{R_{22}} \right] = \nu_{22} \left[1 - \frac{R_{20}}{R_{22}} \right]$$

But as the Rydberg constant is proportional to $\frac{mM}{m+M}$, the reduced mass of the electron, it follows that

$$\frac{R_{20}}{R_{22}} = \frac{m}{m+M_{20}} \times \frac{m+M_{22}}{m}{M_{22}},$$

$$\text{i.e.} \quad \frac{R_{20}}{R_{22}} = \frac{1 + \frac{m}{M_{22}}}{1 + \frac{m}{M_{20}}} = 1 + m \left(\frac{1}{M_{22}} - \frac{1}{M_{20}} \right)$$

to a first approximation. If M is the mass of the hydrogen atom the masses of the neon isotopes are $20M$ and $22M$ respectively, so that

$$\frac{R_{20}}{R_{22}} = 1 - \frac{m}{M} \left(\frac{1}{220} \right)$$

Therefore $\Delta\nu = \nu \frac{m}{M} \frac{1}{220}$ (ν being an approximate mean value of ν_{20} and ν_{22}). It is sufficiently accurate for the purpose to take the mean frequency of the line without consideration of fine structure.)

The ratio $\frac{m}{M}$ is the ratio of the mass of an electron to that of a proton and is equal to $\frac{1}{1836}$, so that

$$\Delta\nu = \nu \frac{1}{1836} \frac{1}{220} = \frac{\nu}{400,000}$$

in approximate round numbers. For a line whose wavelength is 5000 Å the displacement would therefore be about 0.05 cm^{-1} . The isotopic displacement can be calculated for any other line in a similar manner.

The mass isotope displacement effect has been thoroughly investigated in neon and it has been shown that $\frac{\Delta\nu}{\nu}$ is nearly constant for lines of the same series. The value of the displacement is consistently a little greater than that predicted by the simple theory, but the motion of the nucleus accounts for this.

There is no room for doubt that, for each line, the two components are produced by the different isotopes, as Hertz⁸ has clearly shown. In ordinary neon the isotopes are present in the ratio 9 : 1, the lighter atom being the more abundant. The fine structure components should have the intensity ratio 9 : 1, which is observed in practice. Hertz has succeeded in separating the isotopes of neon by means of a continuous diffusion process so that in the two end samples obtained, the ratio of Ne_{20} : Ne_{22} was 1 : 1 and 100 : 1 respectively. The spectrum of the first sample showed each line as a doublet, both components having the same intensity. On the other hand, the second sample showed each line to be quite single, as the other component was too faint. This affords a direct proof of the isotopic origin of the fine structures in neon.

The simple mass isotopic effect is usually very difficult to observe, as it decreases rapidly with increase in atomic

weight. For instance, in the bromine line 6122 Å the displacement should only be 0.004 cm^{-1} . The effect has only been detected in the spectra of $\text{H},^3 \text{Li}, \text{Ne},^4 \text{Cl},^6 \text{K},^6 \text{Br}^4$ (it is doubtful in the last case).

Mixed odd and even isotopes

In the heavy and moderately heavy atoms the simple mass isotope displacement is usually far too minute to be observed. A new effect arises when the atom consists of a mixture of isotopes of even and odd atomic weight. This effect was first observed by Schuler and Brück⁶ in the cadmium spectrum. Cadmium consists of six isotopes, two of which have odd and the other four even atomic weights. The two odd atomic weight isotopes have each a nuclear spin of $\frac{1}{2}$ but no mass displacement can be detected in any of the lines, as the effect is far too small. At the optical centre of gravity of the fine structure of each line lies a single very strong component. Intensity measurements reveal the fact that the intensity ratio of this single component, to the summed intensities of all the other components in the line, is the same as the abundance ratio of the even to the odd isotopes. It was found possible to account for all the components *excluding* the central strong one by assuming $I = \frac{1}{2}$. There seemed to be no doubt about the interpretation of the weak lines, since the number of components and their intensities fitted a spin of $\frac{1}{2}$. It was, therefore, suggested by Schuler and Brück that the even isotopes possess no nuclear spin, so that each contributes a single line, the lines all falling together at the optical centre of gravity of the fine structure pattern and appearing as one. The even isotopes form a single line because the mass displacements are too small to be measured. Obviously the intensity ratio of the central compound component to that of the total sum of the others must be the abundance ratio of the even to the odd isotopes.

The way in which the cadmium fine structures arise is shown in Fig. 18. The line illustrated is $7s^2 \text{S}_1 - 7p^1 \text{P}_1$. Attention may be drawn to the fact that the fine structures in cadmium are inverted, which means that the biggest

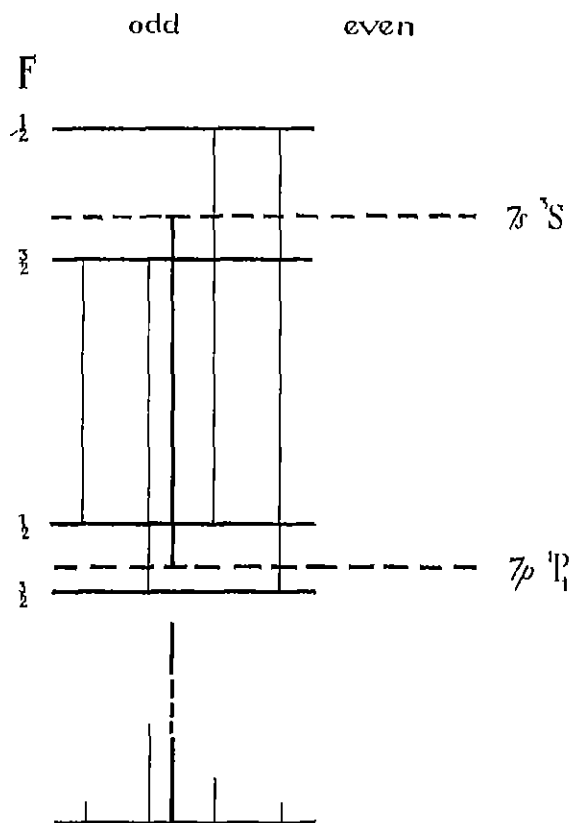


FIG. 18—Undisplaced isotope line due to the even isotopes in the cadmium fine structures. The thin lines show the doublet multiplet due to the odd isotopes, and the thick line represents the unaffected lines from the even isotopes all falling at the centre of gravity of the fine structure pattern.

F values are deepest. *This inversion is not to be confused with the term inversion which was previously discussed when $\cos(I_s) = -1$* The whole of the fine structures are inverted, as if the nuclear magnetic moment arose from a negatively charged nucleus. Referring again to the diagram, the doublet multiplet arising from the split terms of the odd atoms is shown. The quantum weight of a fine structure term is $2F + 1$, so that the dotted lines indicate the centres of gravity of the split terms. The dotted lines are the positions the terms occupy in the even atoms, for obviously the effect of a nuclear spin is to split up a term about its centre of gravity. The thick vertical line represents the transitions in the even atoms, the final resulting line pattern being shown below. It is to be observed that the isotope effect just described only arises from the fact that different isotopes have *different nuclear spins*. There is no displacement of the lines of isotopes which have the same spin.

Isotope displacement effect

The so-called isotope displacement effect is of quite a different nature and was first found in the thallium fine structures by Schüller and Keyston⁹. Thallium consists of two isotopes, 205 and 203, the lighter of which is the more abundant in the ratio 2:3:1. Both isotopes have the nuclear spin of $\frac{1}{2}$. Fig. 19, showing the analysis of the line $6s\ 7s\ ^3S_1 - 6s\ 7p\ ^1P_1$, reveals the displacement effect. The line transitions due to the more abundant isotope, 203, are shown to the left at A, and those due to the less abundant, 205, are shown dotted at B. The observed line pattern is drawn, as usual, below. The analysis was carried out by the use of frequency differences and the careful observation of intensities. Each transition in A is 2.3 times as strong as the corresponding transition in B, so that the analysis is quite certain. Furthermore, there is no doubt about the value of the nuclear spin which has been obtained from other lines which show no isotope effect. The transitions B should fall into the same system as A,

but have been displaced along to the right in order to clarify the diagram

A careful study of the line shows just what the displacement effect is. The structure of the 1P_1 term is the same in both isotopes, but there is a small measurable difference in the widths of the 3S_1 structures. *The most marked effect is the bodily displacement of the whole of the 1P_1 term in one of the isotopes, that is to say, the centre of gravity of the term has been displaced without much appre*

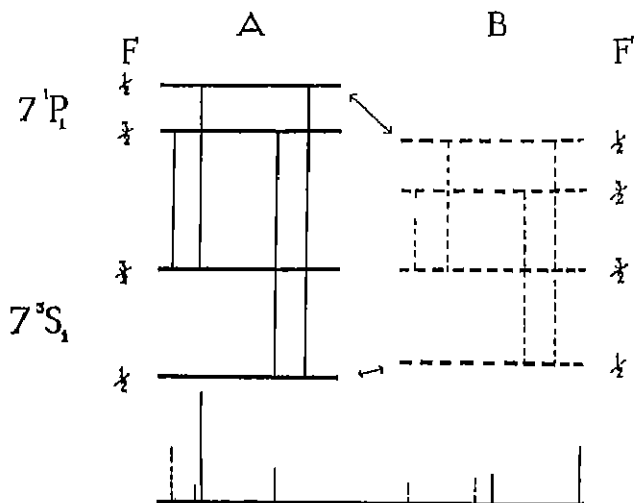


FIG. 19.—Isotope displacement effect in thallium

ciable alteration of the size of the structure. The result of this is a bodily shifting of the whole *line* pattern of the one isotope with respect to the other. The displacement is far greater than that calculated for the simple mass effect and must be ascribed to some other cause. It has been suggested that the electric, and not the magnetic, properties of the nucleus cause the isotope displacement effect, but the motion of the whole nucleus is a more probable cause. This will be discussed later.

Displacement in odd and even isotopes.

Displacements of this type have been observed in mercury and in zinc. The case of mercury is particularly interesting. There are six isotopes of measurable intensity, namely, 198, 199, 200, 201, 202, 204. Both the odd isotopes have nuclear spins, but the point of interest is that the spins differ, that of 199 being $\frac{1}{2}$ and that of 201 being $\frac{3}{2}$. (Other atoms also have different spins for different isotopes.) The fine structure terms in 201 are all inverted relative

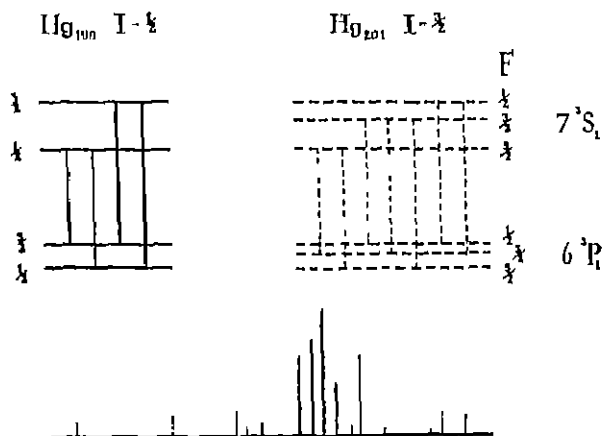


FIG. 20.—Fine structure of the mercury line 4358 Å, showing the isotope displacements. The hatched lines arise from the even isotopes, the dotted lines from 201, and the straight lines from 199.

to those of 199. Some of the terms of mercury illustrate isotope displacement of a more complex nature than that encountered in thallium. Fig. 20 shows an analysis of 4358 Å in Hg I. The four even isotopes do not coincide, as in cadmium, but are relatively displaced (see hatched lines). The observed intensities of these even isotope lines are in excellent agreement with the abundance ratios. The two odd isotopes each show the fine structure pattern

expected from their respective spins, but in addition, the centre of gravity of each pattern is displaced. In the figure the straight lines belong to 199 and the dotted lines to 201. The hatched lines are 198, 200, 202, 204, respectively.

The isotopic displacement effect implies that the binding energies of the electrons are different in different isotopes.

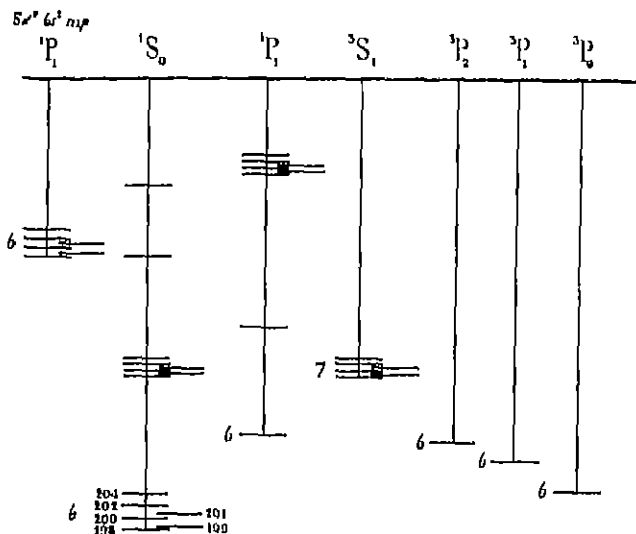


FIG. 21 — Isotope displacements in the terms of the Hg I spectrum. The displacements in all the terms are in the same order as those numbered in 6^1S_0 .

It is natural that different displacements should arise in different terms and a table of the isotopic displacements in the whole of the mercury spectrum reveals facts of great interest. Fig. 21 shows the displacements which have so far been found in the Hg I spectrum¹⁰. The 1S_0 series has big displacements in the deepest term, and these rapidly diminish up the term sequence so that by 8^1S_0 the displacements can no longer be measured. The 7^3S_1 term

also shows a small displacement which diminishes so rapidly up the term sequence that it can no longer be measured in higher terms. Two other terms show a displacement effect, namely the complex 6^1P_1 term arising from the $5d^9 6s^2 mp$ configuration, and the 8^1P_1 term of the ordinary configuration. The complex term is the term shown at the extreme left of the diagram. It follows, therefore, that regular displacements, falling off up a term sequence, only occur in the 1S_0 and 3S_1 terms. The 8^1P_1

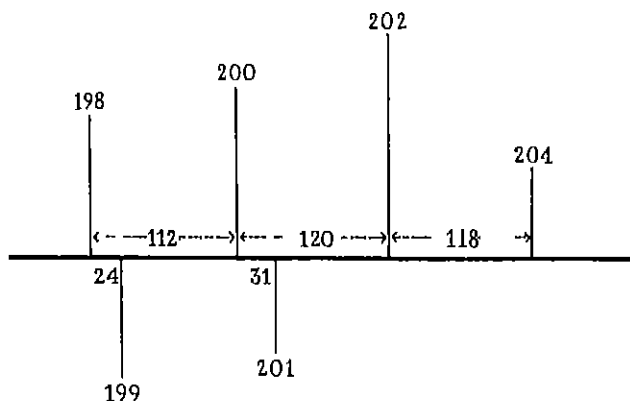


FIG. 22.—Relative displacements of isotopes in the 6^1P_1 term of IIg I.

term shows displacement because it is perturbed. This will be discussed in a later chapter.

The relative displacement of the individual isotopes in one term is also of interest. Fig. 22 shows the displacements arising in the complex 6^1P_1 term. The displacements in all the terms are similar, except that the scales are different. The deepest term is that of 198, and the even isotopes are approximately the same distance apart, in the order of increasing atomic weights. These are shown above the line in Fig. 22. Below the line the centres of gravity of the structures of the odd isotopes are drawn, and

it is seen that although the distance between the centres of gravity is practically identical with the distance between a pair of even isotopes, both the even isotopes are displaced towards the next lightest atom

Dependence of isotopic displacement on electron configuration

In addition to the spectra of IIg I, IIg II, Tl I and Tl II., isotopic displacement has also been found in the spectra of Pb I, Pb II,¹¹ Cu II,¹² Zn II,¹³ Wo I¹⁴ The results can be collected into a table which helps towards obtaining a clearer view of the problem

TABLE VII

Spectrum	Configurations showing displacements
IIg I	6s ms 5d ⁹ 6s ² mp
IIg II	5d ⁹ 6s ²
Tl I	6s ² mp
Tl II	5d ¹⁰ 6s ² 6p
Pb I	6s ² , 6p mp 6s ² 6p md
Pb II	6s ² 6p ² 6s ² 6s 6s ² 6p 6s ² , 6d
Cu II	3d ¹⁰ 4s ²
Wo I	5d ¹ 6s ²
Zn II	3d ⁹ 4s ²

With reference to the table, it should be pointed out that the displacements usually diminish on going up a term sequence. Further, the perturbed terms of IIg I show an anomalous effect, and as perturbations are suspected in the Pb spectra, the data from the latter are as yet somewhat ambiguous. It is interesting to note that a complex term

configuration such as $5d^{10} 6s^2$ mp always seems to give a large isotopic displacement effect. Most of the other terms include an s^2 group, and it may be that this is the cause of the displacement. The complex terms also have an s^2 in their configurations, and it may be possible that some form of quantum mechanical resonance takes place when such a group is present*. This may be perturbed by the nucleus, with an effect depending upon the nuclear mass, so that isotopic displacements proportional to the isotopic masses would take place. Hughes and Eckart¹³ have calculated the mass displacement effect for a many-electron atom, and

TABLE VIII

Hg II Doublet	Hg I Triplet	Tl II Doublet	Tl I Triplet	Pb II Doublet	Pb I Triplet
204 ↑ 198	204 ↑ 198	205 ↑ 203	203 ↓ 205	204 ↓ 208	204 ↓ 208

find that the Bohr formula must be modified by the addition of another term which is proportional to $\frac{1}{M^2}$, where M is the nuclear mass. It appears, therefore, that in heavy atoms the effect of this mass correction would not be sufficient to explain the displacement effects which have been observed. The theory yet remains to be worked out in detail.

A very interesting table has been given by Schüller,¹⁴ who has traced the isotope displacements which occur between the atoms 198 to 208. This table, shown below, illustrates how the isotopic displacement changes in the range from Hg II to Pb I.

* Complex terms are those in which an inner shell is broken by the removal of an electron.

The spectra are alternate doublets and triplets. In the spectra of Hg I. and Hg II the lightest isotope lies deepest and there is a regular upward displacement towards the heaviest isotope. In the spectra of Pb I and Pb II, however, the displacements are still quite regular in the order of atomic weight, but the heaviest isotope lies deepest. Thus in both mercury and lead the directions of the isotope displacements are not affected by the degree of ionisation, and therefore only seem to depend upon the nucleus. The spectra of thallium differ and are particularly interesting, for Tl II, which is next in the sequence to Hg I, has the isotope displacement in the same sense as that of Hg, namely lightest isotope deepest, but Tl I, which is next to the lead group, has its isotopic displacement inverted. It seems as if, in the group comprising the range of isotopes from 198 to 208, there is an abrupt change over from negative to positive displacement. The change apparently occurs at 204, which is isobaric in lead and mercury. The dependence of the isotope shift in thallium upon the degree of ionisation is difficult to account for. The largest isotope displacement in Hg I is about 0.15 cm^{-1} and in the Pb I. spectrum about 0.09 cm^{-1} .

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CHAPTER IX

PERTURBATIONS IN FINE STRUCTURES

IN the present chapter an account will be given of the perturbation effects which have been found in fine structures. Well marked perturbations have been observed in Hg I,¹ Al II,² Bi IV.³ The suggestion has been made by Schüller and Jones that those of Hg I are analogous to the gross structure series perturbations which were first explained by Shenstone and Russell.⁴ From a study of two electron spectra, the latter investigators conclude that in a spectrum with two terms, produced by different electron configurations, but with identical L S and J values, these terms perturb each other, even although they may be widely separated. The perturbation shows itself as an apparent repulsion between the terms. Paschen² and Goudsmit and Bacher⁵ have gone further in the explanation of the effect. It is found that two types of perturbation exist. One is probably similar to the Shenstone-Russell effect, but the other perturbation apparently takes place when the gross structure multiplet separation is of a similar order to that of the fine structure separation. Each will be discussed in turn.

Total widths of the structures

Let us first consider the total widths of the structures which arise from two isotopes of an atom. In most cases when an atom has two odd isotopes, both have the same nuclear spin and the same nuclear magnetic moment μ . In Hg the isotopes 199 and 201 have different spins, namely $\frac{1}{2}$ and $\frac{3}{2}$, the spin being negative in the latter. It can be shown,⁶ that the total splitting of a term, namely the

distance between the extreme F levels for any given gross structure term is ΔW , where

$$\Delta W = \mu H_0 \frac{2J+1}{J} \quad \text{when } J \geq I, \text{ and}$$

$$\Delta W = \mu H_0 \frac{2I+1}{I} \quad \text{when } I \geq J$$

In these formula H_0 is the magnetic field of the optical electron at the nucleus, and only depends on the term, whilst μ is a nuclear function. The ratio of the magnetic moments of 199 and 201, namely μ_{199} and μ_{201} , can be obtained by comparing the total widths of the structures of the two isotopes in a given term. In a particular case,¹ when $J = 1$, for 199,

$$\Delta W_{199} = 3\mu_{199} H_0,$$

and for 201,
$$\Delta W_{201} = \frac{3}{8}\mu_{201} H_0$$

Therefore,
$$\frac{\mu_{199}}{\mu_{201}} = \frac{8}{9} \frac{\Delta W_{199}}{\Delta W_{201}}$$

From five terms with $J = 1$ it was found that the total widths of the structures are identical, but inverted relative to each other, i.e.

$$\frac{\Delta W_{199}}{\Delta W_{201}} = -1,$$

which gives
$$\frac{\mu_{199}}{\mu_{201}} = -\frac{8}{9} = -0.89$$

For terms with $J = 2$ it also follows that

$$\frac{\Delta W_{199}}{\Delta W_{201}} = \frac{\mu_{199}}{\mu_{201}} = -0.89$$

These numerical relations hold well in all the terms examined, except in the 6^1D_1 term, where $\frac{\Delta W_{199}}{\Delta W_{201}} = -0.74$ instead of -1 , and in the 6^3D_2 term, where $\frac{\Delta W_{199}}{\Delta W_{201}} = -1.08$ instead of -0.89 . It is of interest to note that the next

member of the series of the latter term, namely 7^1D_2 , has a normal ratio for the spread of the structures in the two isotopes

The centres of gravity of the structures of lines involving these terms are displaced and this must be connected in some way with the above effect. In lines which do *not* show any appreciably large isotope displacement, the centres of gravity of the structures due to the two odd isotopes practically coincide with the null line formed by all the even isotopes. However, in lines which involve the 6^1D_2 term, the centres of gravity of the structures of the two isotopes practically coincide, *but are both displaced from the null line by an amount roughly equal to 0.04 cm^{-1} , the displacement being to the red*. It will be remembered that $\frac{\Delta W_{199}}{\Delta W_{201}}$, calculated from this term, is too large. On the other hand, in lines involving 6^3D_1 the centres of gravity of the structures due to the two odd isotopes again coincide, but this time *are displaced from the null line to the violet by about 0.06 cm^{-1}* . This term gives too small a value for $\frac{\Delta W_{199}}{\Delta W_{201}}$. Both these anomalies arise from a perturbation which will now be discussed.

Perturbation of F levels

The perturbation in this case arises from the accidental fact that the two terms 6^1D_2 and 6^3D_1 are very close to one another. The structures in these terms are approximately 0.8 cm^{-1} wide and the distance between the centres of gravity of these structures is only 3 cm^{-1} . The whole of the perturbations can be completely explained if it is assumed that *fine structure levels with the same F value repel one another*. The way this perturbation occurs in the 199 isotope is shown in Fig. 23. A very convenient fixed point exists from which the perturbations can be measured, this is the position of the even isotopes. The F value of the even isotope terms in 6^1D_2 is 2 (since $I = 0$) and the F value of the even isotope terms in 6^3D_1 is 1,

and as these F values are different, there is no repulsion effect between the even isotope components. Further there

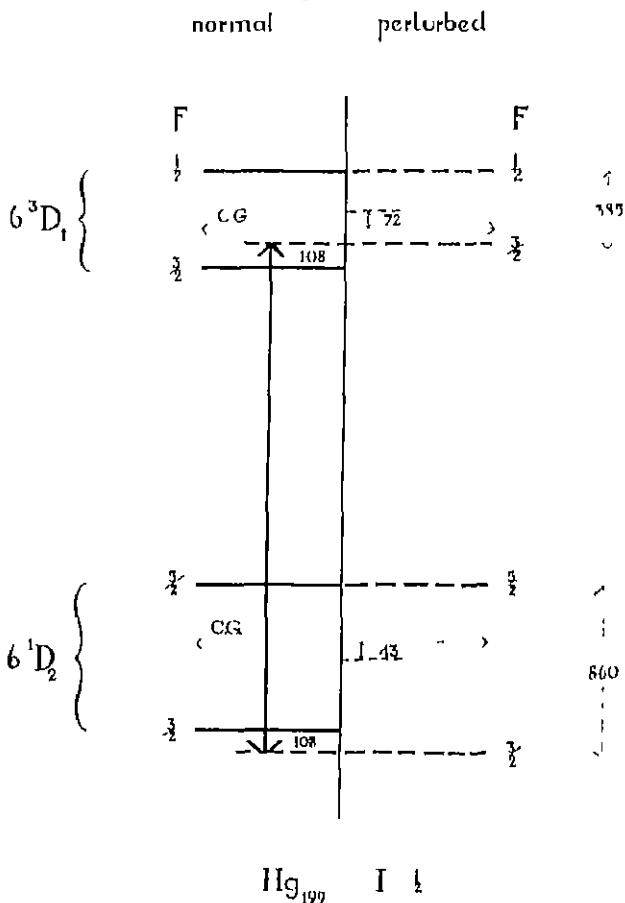


FIG. 23 —Perturbation effect in the 199 isotope of mercury
 is no measurable isotope displacement in both terms, so
 that the even isotopes in both terms form single fixed points.

The fixed points are shown in the diagram by the thin dotted lines which are marked C G, since they are the centres of gravity of the unperturbed terms. Considering now the 199 isotope, the two fine structure levels which have the same F value, in this case $\frac{3}{2}$, repel each other from the zero points by the same amount. The thick lines at the left of the figure show the normal levels, and the dotted lines at the right the perturbed levels. The drawing is to scale, the units * being millicentimetres⁻¹. The thick vertical arrow shows the two levels which repel each other, and it will be observed that, as the upper levels are inverted, the upper structure becomes *narrower*, and the lower structure *wider*. Since the levels of 6^3D_1 shrink together because of the perturbations, the centre of gravity of the fine structure pattern due to Hg_{199} is moved *up* 72 mcms⁻¹. Correspondingly, as the lower term is widened, the centre of gravity of the Hg_{199} pattern is moved *downwards*, in this case 43 units, so that a nett displacement of 29 units, towards the violet, is obtained.

The perturbations in the structures of isotope 201 are a little more complex because the nuclear spin is greater and thus the fine structure multiplicities are also higher. The perturbations are shown in Fig 24, the notation being the same as in the previous figure. For clarity the displacements of the centres of gravity have been omitted. Only the levels with F equal to $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ find their counterparts in both the upper and lower structures, so that the repulsion only takes place between these levels. As in the previous case, the levels with the same F values are both repelled from the unperturbed position by the same amount. For $F = \frac{1}{2}$ the upper level moves up, and the lower down, by a distance equal to $a = 42$ mcms⁻¹. The $F = \frac{3}{2}$ levels displace by $b = 56$ mcms⁻¹ and the $F = \frac{5}{2}$ levels by $c = 78$ mcms⁻¹. *The value of the displacements is such that the interval rule still holds in the upper term structure*, owing to the fact that the lower $F = \frac{1}{2}$ level is not

* A convenient unit to adopt is the millicentimetre⁻¹, which can be written as mcm⁻¹.

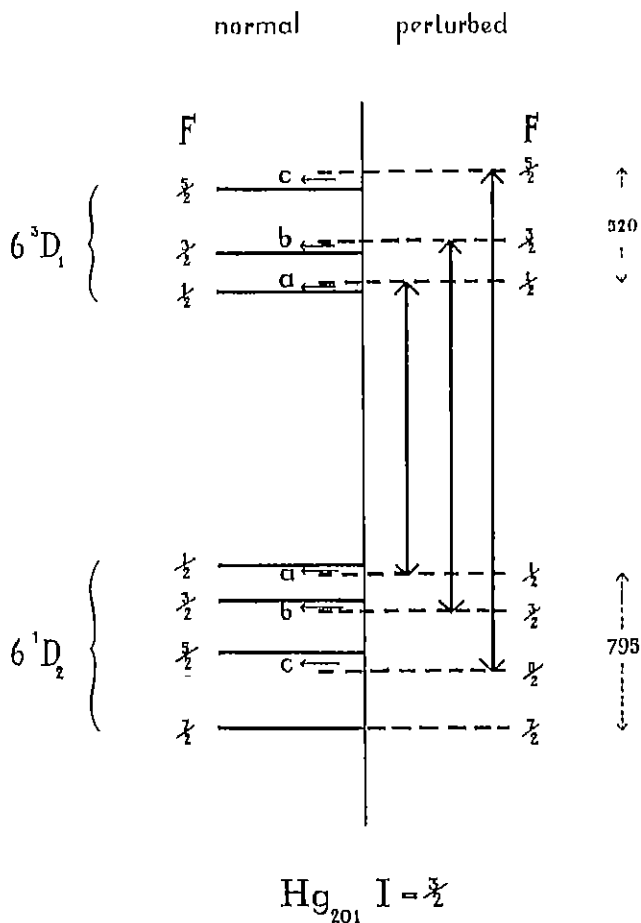


FIG 24 —Perturbation effect in the 201 isotope of mercury, showing how the interval rule breaks down in the perturbed 6^1D_2 term

perturbed the interval rule necessarily breaks down for the lower term as a whole

It is at once apparent from the values of a , b , c that the perturbation is some function of F , and as the perturbation is different in Hg_{100} the effect must also be dependent on the value of I or $g(I)$. Fig. 24 shows that the $F = \frac{1}{2}$ levels are much closer together than the $F = \frac{3}{2}$ levels, yet the perturbation in the latter pair is greater than in the former. Furthermore, the value of the displacement in the $F = \frac{3}{2}$ levels of Hg_{100} is about twice that of the displacement in the $F = \frac{3}{2}$ levels of Hg_{201} , although the latter are nearer together.

The perturbation effect just described explains all the anomalies in the term structures. The values of the total splittings of the terms are so affected that the ratios of $\frac{\Delta W_{100}}{\Delta W_{201}}$ are no longer normal, but the observed values agree with the calculated values when the perturbation is taken into account. The displacements of the centres of gravity of the structures of the odd isotopes are completely accounted for, and the break-down of the interval rule in the 6^1D_2 term of Hg_{201} isotope is thus explained. *Perturbation only seems to take place between levels with the same L and F values*

Isotopic displacement perturbation

Reference to Fig. 21 reveals the interesting fact that the 8^1P_1 term in Hg I has an anomalously large isotope displacement effect in all the isotopes. This is doubtless associated with the fact that this term is perturbed by the $5s^2 6d^9 6p^1 P_1$ term shown at the left of Fig. 21. The whole of the $1P_1$ series of Hg I is perturbed from the 8^1P_1 term upwards, because of the presence of the 6^1P_1 term from the complex configuration. As both terms have the same J value, the even isotopes have the same F value and so perturb each other. The perturbation is proportional to the mass of the atom so that the even isotope lines are regularly displaced. It is possible that some observed isotope displacements are perhaps related to perturbations.

Theory of perturbations

Extensive perturbations in Al II have been observed, and explained by Paschen² According to Paschen, when the coupling between I and J (which determines the total widths of the fine structure pattern of a term) is of the same order as the coupling between L and S (which determines the gross structure multiplet width) then a perturbation sets in. Effectively it is as if the nuclear magnetic field were sufficiently strong to affect the coupling between L and S, and, vice versa, the electron magnetic field perturbs the IJ coupling. (More correctly, it is as if the Paschen-Back effect sets in on both the structures.)

The theory is beautifully verified by Paschen's observations in Al II. By examining successive members of a series, he showed that the perturbations begin to occur when the expected fine structure pattern becomes wider than the multiplet separation. In the term series $4^1F_3 - nG$, the lower series numbers up to 8G show no trace of structure, but beyond this, the terms 8G, 9G, 10G, 11G, show a fine structure practically independent of n . The terms change in character and partake of both singlet and triplet properties. Furthermore the J values are completely undetermined between the values 5, 4, 3. The constancy of the structures is due to the fact that the g electron contributes very little for the high n values, and in effect the structures depend only on the value of the structure of the $3s^2S_{1/2}$ term of Al III, i.e. on the structure of the ion of Al II.

If the above theory is correct, then it can be shown that forbidden lines should appear, i.e. the J selection principle should be violated, and this is found to be the case. Paschen also explains the perturbation in Hg I. as a Zeeman effect. The perturbing terms here are 6^1D_2 and 6^3D_1 , and as long ago as 1902 Runge and Paschen found that these terms showed asymmetrical Zeeman patterns. He is of the opinion that the repulsion effects reported by Schüler and Jones are not a resonance phenomenon, but are just what would take place if the perturbation was a Zeeman effect. Goudsmit

and Bacher⁶ have given a more extended theoretical treatment of the effect. The theory predicts the existence of forbidden transitions when perturbation occurs. Where only two levels of the same F value are apparently repelled, then if δ is the displacement from the null position and if Δ is the actual separation of the two perturbing levels, the ratio of the intensity of forbidden transitions I to allowed

transitions I_0 is given by the formula $\frac{I}{I_0} = \frac{\delta}{\Delta + \delta}$. In

Hg I this is only true for the odd isotope terms, for there is no perturbation in the even isotopes. It follows from the theory that transitions should take place from 6^1D_2 to terms with $J = 0$, and from 6^3D_1 to terms with $J = 3$. It is of particular interest that the line $6d \cdot ^1D_2 \rightarrow 7p \cdot ^3P_0$ actually occurs and when examined for fine structure it is found that the even isotopes are entirely missing.⁷ This is a valuable proof of the theory, which demands forbidden transition in the odd isotopes only.

Intensity perturbations

The intensities in fine structure components can, of course, be modified by self absorption, but this cannot be regarded as a true perturbation effect. Intensity perturbations have only been found in a hollow cathode discharge in cadmium when the exciting currents are high.⁸ In certain lines the transitions which involve the highest F value of the upper term are relatively strengthened. This effect is not due to self absorption, and has not yet been explained.

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CHAPTER X NUCLEAR SPINS

TABLE IX

Atom	Atomic weight	Nuclear spin	Reference	Atom	Atomic weight	Nuclear spin	Reference
H*	1	$\frac{1}{2}$	1	Cd	110	0	21
H*	2	1	33		111	$-\frac{1}{2}$	
He*	4	0	3		112	0	
Li*	6	0(?)	2		113	$-\frac{1}{2}$	
	7	$\frac{3}{2}$			114	0	37
C*	12	0	3	In	115	$\frac{1}{2}$	
N*	14	1	4	Sn	116	0	
O*	16	0	3		117	$-\frac{1}{2}$	
F*	19	$\frac{1}{2}$	5		118	0	38
Ne	20	0	6		119	$-\frac{1}{2}$	
	22	0			120	0	
Na*	23	$\frac{3}{2}$	7	Sb	121	$\frac{3}{2}$	22
Mg	24	0	8		123	$\frac{1}{2}$ or $\frac{3}{2}$	
Al	27	$\frac{3}{2}$	9	I	127	$\frac{5}{2}$	42
P*	31	$\frac{1}{2}$	10	Xe	129	$-\frac{1}{2}$	39
S*	32	0	3		131	$\frac{3}{2}$	
Cl*	35	$\frac{3}{2}$	11	Cs	133	$\frac{7}{2}$	23
K*	39	$\frac{3}{2}$	12	Ba	135	$\frac{3}{2}$	24
Ca	40	0	13		136	0	
Mn	55	$\frac{5}{2}$	14		137	0	
Fe	56	0	15		138	0	
Cu	63	$\frac{3}{2}$	16	La	139	$\frac{7}{2}$	25
	65	$\frac{3}{2}$		Pr	141	$\frac{5}{2}$	26
Zn	64	0	34	Ta	181	$\frac{7}{2}$	40
	66	0		Re	185	$\frac{5}{2}$	27
	67	$\frac{1}{2}$			187	$\frac{5}{2}$	
	68	0		Au	197	$\frac{3}{2}$	16
Ga	69	$\frac{3}{2}$	17	Hg	196	0	28
	71	$\frac{3}{2}$			198	0	
As	75	$\frac{3}{2}$	18		199	$\frac{1}{2}$	
Br	79	$\frac{3}{2}$	19		200	0	
	81	$\frac{3}{2}$			201	$-\frac{1}{2}$	
Kr	83	$\frac{1}{2}$	35		202	0	
Rb	85	$\frac{5}{2}$			204	0	29
	87	$\frac{5}{2}$	20	Tl	203	$\frac{1}{2}$	
	87	$\frac{1}{2}$			205	$\frac{3}{2}$	
Sr	88	0	36	Pb	204	0	
					206	0	31
					207	$\frac{1}{2}$	
					208	0	
				Bi	209	$\frac{9}{2}$	32

The table contains all the values of the nuclear spins known up to date. A list of authorities has been quoted, but this is not meant to be complete, since many papers have often been published on one atom. Some of the more important papers are given, and cross references in the papers themselves will easily lead to the rest. The asterisk indicates those atoms wherein the spin has been deduced from band spectrum observations. It is apparent from the table that, with the exception of nitrogen and the rare H^3 isotope, all the observed even atomic weight atoms possess a nuclear spin of zero. Without band spectrum observations, it is impossible to tell whether the absence of fine structures is due to a zero nuclear spin or to a small $g(I)$ factor. It follows that the zero values are only quite certain in the cases where band spectrum observations have been carried out, a doubt always remaining in the others. There seems to be very little regularity in the values of the spin. Schüller and Kallman⁴¹ have attempted to show that an elementary regularity exists, and they concluded that high nuclear spins are only associated with single isotopes, and that, excluding mercury, in any atom with two odd isotopes, both have the same spin value. Additional data have appeared since these regularities were proposed, it has been found that krypton (with many isotopes) has a spin of $> \frac{1}{2}$, whilst Hg, Xe and Rb possess two odd isotopes and have different spins. Very abrupt changes in spin value take place when moving from one odd atom to the next, and negative and positive values do not appear to be in special groupings.

Not all the values given in the table are known with the same degree of certainty. Particular difficulty is experienced with high and with zero values. When I is large the complete fine structure multiplicity is only reached when $J > I$, and this is usually very rare. Hence intensity measurements, or the interval rule, must decide the I value, and it is often difficult to obtain an unambiguous determination. The question of zero spin with most even isotopes still remains open. The subject will be discussed in the chapter on nuclear magnetic moments.

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CHAPTER XI

NUCLEAR MAGNETIC MOMENTS

Magnetic and mechanical moments

We have already seen that the number of fine structure levels in a term depends upon the value of I (provided that $I > J$). The width of the structure is determined, not by the *mechanical* moment, but by the *magnetic* moment of the nucleus. The effect of the nuclear mechanical spin is to create a nuclear magnetic field, which, coupling with the magnetic field produced by electron spin and orbital moment, gives the observed fine structure pattern. The coupling theory has been dealt with in earlier chapters, but it is at once apparent that the size of the structure is dependent on the value of the nuclear magnetic moment. It will be shown later that in favourable cases this moment can be calculated from the observed fine structure patterns.

It will be recalled that the phenomenon of alternating intensities in band spectra arises from the existence of the *mechanical* moment I , whilst the widths of the fine structures in the line spectra depend (amongst other things) upon the *magnetic* moment, i.e., on $g(I)$ (see page 37). Cases occur where an atom has a definite value of I as revealed by the band spectrum, yet no fine structures are observable, even in terms involving penetrating electrons. The conclusion must be made that the nuclear magnetic moment is small, so that no measurable structures exist. Associated with this is the problem of the reported zero spins for so many even isotopes. All that has really been observed, in *line* spectra, is that the even isotope lines show no structure. Band spectrum observations in He^4 , C^{12} , O^{16} , S^{32} , prove that these four even atoms have zero spin, but attention

may be drawn to the fact that these atomic weights are divisible by four. The assumption has been made that because these four even atoms are known to possess a zero spin, therefore the absence of structure in other even isotope lines is also an indication of zero spin. This may not be true. It is quite possible that some even isotopes may have a mechanical spin but have extremely small nuclear magnetic moments. This is certainly the case with N^{14} and with H^2 . This point cannot be over-emphasised, for unfortunately a tendency has grown up in which workers have unquestioningly assumed that absence of structure in even isotopes means zero spin.

Magnetic moment of the proton

The value of the magnetic moment of the proton is of particular interest, for it will later be shown that theories of nuclear spin have been proposed which attribute the nuclear magnetic properties to protons and neutrons. It is apparent from the relatively small values of the nuclear spins ($\frac{1}{2}$ is the greatest observed with certainty) that only a very limited number of the nuclear protons or neutrons contribute to the spin. It may be possible, therefore, to correlate the value of the proton or neutron magnetic moment with nuclear magnetic moments in general, and indeed attempts to do this have been made¹. A value of the magnetic moment of the proton can be deduced from very simple considerations. Both electron spin and proton spin are $\frac{1}{2}$, but as the protonic mass is 1836 times as great as the electronic mass, the magnetic moment of the spinning proton should be $\frac{1}{1836}$ that of the electron, i.e. $\frac{1}{1836}$ of a Bohr magneton. It has been pointed out before that the doublet separation in gross structure multiplets is due to the *electron* magnetic moment, so that on this basis, to a first approximation, fine structures should be 2000 times smaller than the gross structure width.

The magnetic moment of the proton has recently been determined experimentally by Estermann and Stern² by means of a very refined improvement of the Stern-Gerlach experiment. In this experiment a beam of atoms or molecules is

passed through an intense non-homogeneous magnetic field, and the deflections that the beam experiences enable the magnetic moment of the particles of the beam to be calculated. Molecular hydrogen exists in two states, para and ortho, in one of which the electron spins oppose and in the other assist. A beam of hydrogen was used in which the electron spins cancel out, so that the magnetic moment due to the protons could be observed, and it was found that the proton magnetic moment was 2.5 (± 10 per cent) times that expected, i.e. $\frac{2.5}{1836}$. Thus if the magnetic

moment is μ and the nuclear spin I , then $\mu = I g(I)$, providing the correct units are employed. μ is expressed in theoretical proton magnetons $\frac{eh}{4\pi Mc}$, that is to say, the Bohr electron magneton divided by the nuclear mass M . By analogy with the electron g value, one expects for a proton that $I = \frac{1}{2}$ and $\mu = 1$, so that $g(I)$ would be 2. Experiment, however, shows that μ for the proton is 2.5, so that $g(I) = 5$.

The magnetic deflection method of calculating the magnetic moments has, so far, only been used in a few cases. It is very important, since it is a direct method, and it is to be hoped that it will be extended in the near future.

Calculation of nuclear magnetic moments.

The calculation of nuclear magnetic moments from the data of hyperfine structure has been given by Goudsmit.⁴ As we have already seen, the coupling energy between electron and nucleus determines the total splitting, and this is given by

$$W = A \mathbf{I} \cdot \mathbf{J} \cos(\mathbf{I} \cdot \mathbf{J}) = \frac{1}{2} A [F(F+1) - J(J+1) - I(I+1)].$$

When an alkali-like spectrum (a single optical electron) is under consideration, then the interval factor A is that of the optical electron a .

Coupling theory shows that

$$a = \frac{R\alpha^2 z^3}{n^3(1 + \frac{1}{2}j)(j + 1)} \frac{g(I)}{1836} \text{ cms}^{-1}$$

In this formula R is Rydberg's constant, α^2 is the spectroscopic doublet constant, z is the nuclear charge, n the total quantum number, l and j have the usual significance, and $g(I)$ is the numerical ratio of the magnetic to mechanical moments

When the case of a penetrating electron is considered, the formula is altered and a relativity correction has to be applied. The final formula for the $g(I)$ factor in the case of a penetrating s electron is

$$g(I) = \frac{a}{8R\alpha^2} \frac{n_0^3}{Z_i z_0^3} \frac{1836}{K(jZ_i)}$$

It will be seen that only two changes have really been made. n_0 is the effective total quantum number of the term, which is easily obtained if the absolute term value is known. z^3 has now been replaced by $Z_i z_0^3$, in which z_0 is the effective nuclear charge in the outer portion of the electronic orbit and Z_i is the average effective nuclear charge when the electron is passing through the inner penetrating portion of the orbit. For a neutral atom $z_0 = 1$, for a singly ionised atom $z_0 = 2$, etc. In heavy atoms and deeply penetrating orbits the electron approaches so closely to the nucleus that practically all the screening effect of the outer electrons is reduced to zero. The effective Z_i may thus be taken as approximately equal to the atomic number. The relativity correction $K(jZ_i)$ depends upon j and Z_i , and a table of values for K has been calculated by Goudsmit.

As an example of applying the formula, the following calculation of the $g(I)$ factor of tin will now be given.

The nuclear spin of tin is $\frac{1}{2}$ and the $6s^2 5p^2$ term (odd isotopes) is a doublet 0.207 cms⁻¹ wide. The F values of the fine structure levels are 1 and 0, so that the fine structure separation is the interval factor. Hence

$$A = a = -0.207 \text{ cm}^{-1}$$

The n_0 for $6s \ ^2S_{1/2}$ in tin is 2.685, and $R = 109,737$. The effective inner charge Z_i is 50, which is the atomic number of tin, and as the Sn II spectrum is under consideration, $z_0 = 2$. The relativity correction for $j = \frac{1}{2}$ and $Z_i = 50$ is 1.30, and the spectroscopic doublet constant has the value 5.305×10^{-5} . On substituting these data, one obtains $g(I) = -1.78$. Since $I = \frac{1}{2}$, and as $\mu = I g(I)$, the nuclear magnetic moment is -0.89 Bohr proton magnetons, or $\frac{1}{1836}$ that of the electron.

The formula utilised above is only to be used with s electrons, and when other relatively non-penetrating orbits are studied, a different formula is required, and has been deduced by Goudsmit as follows —

$$g(I) = \frac{aZ_i j(j+1)(1+\frac{1}{2})}{\Delta\nu \ I(1+1)} \frac{\lambda(IZ_i)}{K(jZ_i)} \quad 1836$$

$g(I)$, a , Z_i , j , I , K , have their previous meanings, $\lambda(IZ_i)$ is a relativity correction depending upon the I value, i.e. on whether p , d , or f electrons are involved. $\Delta\nu$ is the spin doublet separation. Thus, if a $6p$ electron is under review, then $\Delta\nu$ is the separation between $6p \ ^2P_{3/2}$ and $6p \ ^2P_{1/2}$, and similarly for other electrons. With p electrons, Z_i is not equal to the atomic number Z , but throughout the periodic table it has always been found that $Z_i \approx Z - 4$. As this is always a little uncertain, the $g(I)$ values calculated from p electrons may be too small.

When the terms arise from complex electron configurations, the separate electron interval constants (see page 63) must be obtained before the $g(I)$ factor can be calculated. Uncertainty often arises here, so that many calculated $g(I)$ factors are only approximate.

Observed $g(I)$ factors

Since the magnetic moment μ is $I g(I)$, and as I differs from atom to atom, a table of $g(I)$ factors may be more useful than a table of μ values. Most of the values given in the following table have been calculated by Goudsmit.⁴

TABLE X
Atomic $g(I)$ Factors

Atom	Isotope	$g(I)$	Reference	Atom	Isotope	$g(I)$	Reference
H	1	5	2	In	115	1.2	4
	2	<2.5	3	Sn	117	-1.78	5
Li	7	2.19	4		119	-1.78	5
N	14	<0.2	6	Sb	121	1.1	4
Na	23	1.4	4		123	0.6	4
Al	27	4.2	4	Cs	133	0.75	10
Cu	63	1.7	4	Ba	137	0.6	10
	65	1.7	4	Hg	199	1.1	4
Ga	69	1.34	4		201	-0.41	4
	71	1.70	4	Tl	203	3.6	4
As	75	0.6	4		205	3.6	4
Rb	85	0.5	4	Pb	207	1.2	4
	87	1.8	4	Bi	209	0.89	4
Cd	111	-1.33	4				
	113	-1.33	4				

In addition to the table it may be mentioned that Kr⁷ has two isotopes whose magnetic moment ratio is -1.1 and also that Sr₈₇ has a larger⁸ magnetic moment than its isobar Rb₈₇.

Two other facts of interest are connected with the magnetic moments of the nuclei. The first is that a group possess negative spins, that is to say the magnetic moments associated with these nuclei are such as if negatively charged nuclear particles and not protons were responsible. The nuclear spin interacts with the J values to give completely inverted fine structure patterns. Table XI shows the atoms known to have negative spin —

TABLE XI

Atom	Hg	Xe	Sn	Sn	Cd	Cd	Sr	Kr
At weight	201	129	119	117	113	111	87	83
Spin	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$>-\frac{1}{2}$	$>-\frac{1}{2}$

The second fact of interest in connection with the nuclear magnetic moments is that several atoms appear to have

abnormally small $g(I)$ factors⁹ For instance nitrogen, phosphorus, chlorine, potassium and silver show no trace, or almost no trace, of fine structure in their spectra, although the lines examined involved penetrating electrons in each case On the other hand, the band spectra of the molecules of these atoms show the phenomenon of alternating intensities, and measurements of the nuclear *mechanical* moments have been made from these It follows that although these atoms have quite definite nuclear *mechanical* spins (in Cl it is as high as $\frac{3}{2}$) yet the nuclear *magnetic* moment must be very small, otherwise fine structures would be visible These anomalously small $g(I)$ factors will have to be taken into consideration in any complete theory of nuclear spin

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CHAPTER XII

THEORIES OF NUCLEAR SPIN

General considerations

At the present time it is generally considered that the nuclear constituent particles are α particles, protons and neutrons, in addition there is clear evidence of the existence in nature of positive electrons. Many different theories have been proposed, with the object of accounting for nuclear spins, but the difficulties are great and advance has been slow. It has long been known that the proton has a spin of $\frac{1}{2}$ and Table IX shows that half integral nuclear spins are invariably associated with odd atomic weights. Heisenberg¹ is of the opinion that all nuclear electrons are bound up to protons in the form of neutrons. It has been shown theoretically, that the electron when inside the nucleus loses its spin,² and Heisenberg concludes that the neutron retains the same mechanical spin as the proton, namely $\frac{1}{2}$. Since the nuclear spin of the helium atom is zero, it follows that α particles have zero spin, and as nuclei are composed of α particles, protons and neutrons, the nuclear mechanical moment must arise from neutrons or protons, or both.

The most striking fact about the nuclear spin values is that, although a heavy atom must be built up out of a very large number of particles, yet the greatest spin observed is $\frac{9}{2}$, and the majority are much smaller. This proves that only a few of the nuclear particles contribute to the spin. Two suggestions have been made to explain this. The first is, that in the nucleus, closed proton and neutron shells exist analogous to closed outer electron shells. On this view it is only the outer unbound neutrons, or protons,

which contribute to the nuclear mechanical and magnetic moments. The second view is that practically all the neutrons and protons unite to form α particles where possible, and only the odd one produces the spin properties.

Proton-neutron configurations

Some preliminary attempts have been made by White³ and by Bryden⁴ to give a theory of nuclear spins on the basis of proton-neutron configurations. Both these authors assume that each particle has a spin of $\frac{1}{2}$ and, in addition, an orbital angular momentum exactly analogous to electronic orbits. They assume that nuclear particle shells will be built up in the same manner as electron shells. There will be s nuclear particles with l value 0, p particles with l value 1, etc. On this basis a table of nuclear particle configurations can be built up. This will result in "nuclear terms" and the comparison of the J values of the deepest term in each configuration seems to agree with the nuclear spin. It was, therefore, proposed that the nuclear spin I is actually the equivalent of the J of the electron system. The table, due to White, is shown below and it will be seen that no attempt is made to distinguish between proton and neutron.

TABLE XII

Atom	Configuration	Deepest state	Spin
H ¹	1s		$\frac{1}{2}$
He ⁴	1s ² 2s ²		0
Li ⁷	1s ² 2s ² 2p ³		$\frac{3}{2}$
C ¹²	1s ² 2s ² 2p ⁰ 3s ²		0
N ¹⁴	1s ² 2s ² 2p ³ 3s ² 3p ³		$\frac{3}{2}$
O ¹⁶	1s ² 2s ² 2p ⁴ 3s ² 3p ⁴		0
F ¹⁹	1s ² 2s ² 2p ⁰ 3s ² 3p ⁶ 4s		$\frac{1}{2}$

A more general configuration system has been proposed by Gapon and Iwanenko,⁵ and by Bartlett.⁶ Heisenberg⁷ showed that nuclear particles require *five* quantum numbers to describe them, and from this it follows that the number

of particles in a shell is not $2(2l + 1)$ as in extra nuclear system (which is assumed above) but should be $4(2l + 1)$. Gapon and Iwanenko therefore assumed that closed shells are formed, as in extra-nuclear electron systems, but that each contains $2(2l + 1)$ neutrons and $2(2l + 1)$ protons.

Starting with an α particle as the beginning, then up to O^{16} alternate neutrons and protons are added, and it is found that one obtains only the isotopes known to exist in nature. A new shell begins at O^{16} and after this neutron, neutron, proton, proton, are added up to A^{30} , and again only existing isotopes are predicted. As an example, the first group is shown in the table. In the arrangement α particles have lost their identity, but the compound group of two neutrons and two protons remains important. It has not yet been found possible to predict nuclear spins unambiguously from this table. N and P represent neutron and proton respectively.

Shell	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P	N P
1s	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2
2s		1	1 1	2 1	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2	2 2
2p						1	1 1	2 1	2 2	2 2	3 2	3 3	4 3	4 4	5 4				
Atom	He ⁴	He ⁴	Li ⁶	Li ⁷	Be ⁸	Be ⁹	B ¹⁰	B ¹¹	C ¹²	C ¹³	N ¹⁴	N ¹⁵	O ¹⁶	O ¹⁷					

Single particle theory

The theory that the spin is due to a single particle has been put forward by Landé.⁸ There are two types of odd atomic weight atoms, namely those in which the nuclear charge is odd, and those in which it is even. Heisenberg considers that the nuclei of the first group possess α particles, an even number of neutrons, and one unbound proton, whilst the second group possess α particles and an odd number of neutrons, that is, at least one unbound neutron. For the first group Landé assumes that the single odd

unbound proton is entirely responsible for the total nuclear mechanical and magnetic moments. The spin of the proton is $\frac{1}{2}$, and this may combine with the orbital angular momentum l to form the nuclear spin I such that I may be either $l + \frac{1}{2}$ or $l - \frac{1}{2}$. From this Landé shows that the $g(I)$ factor is given by

$$g(I) = g_l \left[\frac{l(l+1) + I(I+1) - s(s+1)}{2I(I+1)} \right] + g_s \left[\frac{s(s+1) + I(I+1) - l(l+1)}{2I(I+1)} \right]$$

In this formula $s = \frac{1}{2}$ is the proton spin, and g_l must be 1, g_s is the magnetic factor of the proton, and according to the Stern-Gerlach experiment should be approximately 5 ± 0.5 . Landé finds, however, that if he takes it as equal to 4 he can predict with a fair degree of certainty a number of the experimentally observed factors. On substituting values in the above formula he obtains the following table of $g(I)$ factors —

TABLE XIII

	I	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$
1						
0		4				
1		0	2			
2			$\frac{2}{3}$	$\frac{2}{3}$		
3				$\frac{2}{3}$	$\frac{1}{7}$	
4					$\frac{1}{7}$	$\frac{1}{11}$
5						$\frac{1}{11}$

It is obvious that any nuclear spin I can only arise from one of two l values, namely $I \pm \frac{1}{2}$. It is then an easy matter to select the $g(I)$ factor which fits closest to the experimental value, and no ambiguity arises, one value being more, and the other less than unity. The result of applying this to the observed $g(I)$ factors is shown in the following table —

TABLE XIV

Atom	Spin	$g(I)$ observed	$g(I)$ calculated	I value
Li^7	$\frac{1}{2}$	2.19	2	1
Al^{27}	$\frac{5}{2}$	4.2	4	0
$\text{Cu}^{63, 65}$	$\frac{3}{2}$	1.7	2	1
Ga^{69}	$\frac{3}{2}$	1.34	?	
Ga^{71}	$\frac{3}{2}$	1.70	?	
As^{75}	$\frac{3}{2}$	0.6	0.4	2
Rb^{85}	$\frac{5}{2}$	0.5	0.57	3
Rb^{87}	$\frac{5}{2}$	1.8	2.0	1
In^{115}	$\frac{5}{2}$	1.2	1.33	4
Sb^{121}	$\frac{5}{2}$	1.1	1.6	2
Sb^{123}	?	0.6	0.57	3
$\text{Tl}^{203, 205}$	$\frac{5}{2}$	3.6	4	0
Bi^{209}	$\frac{9}{2}$	0.89	0.71	5

Considering the imperfection of the theory used in the calculation of the value of $g(I)$, and the uncertainty in the value of g_s for the proton, the agreement between observation and prediction is very good in most cases. There are certain exceptions which necessitate a further assumption which will be discussed later.

The above theory has been extended to include the other type of odd atomic weight atom, namely that in which the nucleus has an odd number of neutrons.⁹ In this case the g_l factor is obviously zero, for the neutron has no magnetic moment due to its orbital motion. The best fit with the observations is obtained if the spin g factor for the neutron g_s is taken as -1.2 . This means that the neutron has a negative magnetic moment of $-1.2 \times \frac{1}{2} = -0.6$ magnetons. When $g(I)$ factors are calculated on this assumption, it is found that they are sometimes positive and negative, as shown in Table XV.

It follows that the difficulty about the existence of negative nuclear spins disappears. Actually, however, it has been found necessary to modify the theory somewhat, and to assume that in some cases as many as three nuclear particles can contribute to the spin. Tamm and Altschuler¹⁰

consider that sometimes a pair of neutrons does not form a closed shell with zero spin, but add up to give a spin of 1. This spin then combines with that due to the remaining odd proton or neutron, as the case may be, and if the latter,

TABLE XV

$\begin{smallmatrix} I \\ \backslash \\ 1 \end{smallmatrix}$	$\frac{1}{2}$	$\frac{3}{2}$
0	- 1 2	
1	+ 0 4	- 0 4
2		+ 0 2 1

the three neutrons always give a spin of $\frac{3}{2}$. This assumption doubles the possible number of $g(I)$ factors that can be calculated for a given nuclear spin, as shown in the Table XVI below —

TABLE XVI

$\begin{smallmatrix} I \\ \backslash \\ 1 \end{smallmatrix}$	$\frac{1}{2}$	$\frac{3}{2}$
0	- 1 2	- 1 2
1	+ 0 4 - 2 0	- 0 4 - 0 8 8
2	+ 1 2	+ 0 2 4 - 0 2 4
3		+ 0 7 2

Comparison between the theoretical and experimental values is made in Table XVII

In those atoms with the nuclear s value $\frac{1}{2}$ only a single neutron contributes, whilst in the cases where $s = \frac{3}{2}$ three neutrons are involved

This theory is, of course, as yet incomplete, but so far the results agree to a surprising degree with the observed

values The value adopted for the magnetic moment of the proton, namely 2 magnetons, differs somewhat from the value 2.5 obtained by the Stern-Gerlach experiment

TABLE XVII

Atom	I	g(I) observed	g(I) calculated	I	g
Cd ₁₁₃	$\frac{1}{2}$	-1.26	-1.20	0	$\frac{1}{2}$
Hg ₂₀₁	$\frac{1}{2}$	-0.41	-0.4	1	$\frac{1}{2}$
Sn ₁₁₉	$\frac{1}{2}$	-1.90	-2.0	1	$\frac{1}{2}$
Ba ₁₃₇	$\frac{1}{2}$	+0.63	+0.72	3	$\frac{1}{2}$
Hg ₁₈₀	$\frac{1}{2}$	+1.10	+1.2	2	$\frac{1}{2}$
Pb ₂₀₇	$\frac{1}{2}$	+1.20	+1.2	2	$\frac{1}{2}$

on *molecular* hydrogen rays, and from the value 3.2 given by *atomic* hydrogen rays. Of great interest is the fact that the neutron possesses a negative magnetic moment, that is such as would be produced by a negatively charged particle.

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APPENDIX I

FINE STRUCTURE ZEEMAN EFFECT

THIS will be only described very briefly, more detail being given elsewhere¹. The complete Paschen-Back effect is the simplest to consider. In this, the external magnetic field is so strong that its coupling with \mathbf{I} and \mathbf{J} is great enough to break the mutual interaction of \mathbf{I} and \mathbf{J} . It can be shown that, to a first approximation, the Zeeman pattern is the same as that of an atom when no nuclear spin is considered, that is to say, the line will be split up into its usual Zeeman components. The introduction of a nuclear spin affects each of these Zeeman components slightly and this can sometimes be detected. The total interaction energy of the atom with the field H is

$$w = O[m_I g(I) + m_J g] + A \mathbf{I} \cdot \mathbf{J} \cos(\mathbf{I} \cdot \mathbf{J}),$$

where O is the Lorentz unit $\frac{ehH}{4\pi m_0 c}$, g is the ordinary electronic g factor, $g(I)$ the nuclear factor, and m_I and m_J the projections of \mathbf{I} and \mathbf{J} along H . Averaging the cosine term reduces the expression to

$$m_J(Og + Am_I)$$

m_I can assume any of the $2I + 1$ integral or half integral values between $+I$ and $-I$. Hence, each Zeeman level, which without the spin is single, now splits up into $2I + 1$ components equally spaced by the distance Am_J . The only transitions allowed are those in which m_I does not change, so that each gross Zeeman line splits into $2I + 1$ fine structure Zeeman lines. For two terms J and J' the separations will be $Am_J - A'm_{J'}$. The A and A' values can be calculated from the fine structure, which

arise when there is no magnetic field, and $m_l = \pm \frac{1}{2}$ for both states when parallel components arise. Hence, the separation can be predicted. The components gives the simplest and most satisfactory of obtaining the nuclear spin. Thus, in Bi I, Zeeman theory was beautifully verified, each ground component consisted of 10 lines. As this is $2I + 1 = 10$.

If incomplete Paschen-Back effects exist, it becomes extremely complicated, but the experimental evidence seems to agree very well with theory, to the extent that the normally forbidden transition is to be expected when external fields are applied.

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APPENDIX II

OTHER EXPERIMENTAL METHODS

VERY brief mention will be made here of two very recent methods of obtaining nuclear spin data by means other than that of fine structure

(a) From the study of the polarisation of resonance radiation¹ it has been found possible to calculate the unresolved fine structures occurring in the upper terms of the sodium D lines. The separation given is extremely small and of the order of $5 \times 10^{-4} \text{ cm}^{-1}$, a separation totally impossible to resolve by spectroscopic means. From investigation of the Paschen-Back effect of the polarised resonance radiation, Heydenburg and Ellet² are able to find the magnetic moment of sodium as $\frac{2.5}{1840}$,

whilst fine structure data give $\frac{2.8}{1840}$, which is a highly satisfactory agreement.

(b) By a refinement of the Stein-Gerlach experiment it has been found possible to calculate nuclear spins, and Rabi and Cohn have succeeded in finding the nuclear spin of a number of atoms by this method.³ An atomic beam is passed through an inhomogeneous magnetic field and from the shape of the Stein-Gerlach pattern, the nuclear spin can be calculated.

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